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Most assuredly, time has not abated one whit of the fluency, the vigor, and the clearness with which they not only have composed the work before us, but have, so to say, cleared the ground for it, by hitting right and left at the affectation, mysticism, and obscurity which pervade some late chemical treatises. Thus conceived, and worked out in the most sturdy, common sense method, this book gives, in the clearest and most summary method possible, all the facts and doctrines of chemistry, with more especial reference to the wants of the medical student.—*London Medical Times and Gazette*, Nov. 29, 1862.

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An elementary treatise from two of our most veteran teachers and greatest authorities on chemistry, compels a welcome reception. There is a novelty in this book of Drs. Brande and Taylor which will doubtless secure for it a principal place among text-books for chemical students. Of the execution of this work as conceived by the authors it is idle to speak. Their names alone are a sufficient guarantee for its completeness.—*The Medical Critic*, Jan. 1863.

CHEMISTRY.

BY

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EXPERIMENTIS ET PRÆCEPTIS.

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AMERICAN PUBLISHERS' NOTICE.

In order to secure the accuracy of the present volume, its passage through the press has been superintended by a competent chemist. No notes or additions have been introduced, but the publishers have been favored by the authors with some corrections and revisions of the first twenty-one chapters, which have been duly inserted.

Philadelphia, April, 1863.

PREFACE.

THE Student of CHEMISTRY has already a large selection of books for his guidance. In the "FIRST STEP" of Mr. Galloway, of about ninety pages, and in the translated "HANDBOOK" of Gmelin, as yet incomplete, but filling, at the present date, fourteen octavo volumes, and covering nearly eight thousand pages—we have the two extremes of English Chemical literature. There are numerous books on the Science, which occupy an intermediate position, some, under the title of "Elements," treating the subject so profoundly as to alarm a beginner; while others are so filled with symbols, formulæ, and mystical language, as to conceal the great facts of Chemistry in a haze of technicality.

We see no reason for adopting an esoteric method of dealing with this Science. On the contrary, it appears to us, that without departing from the true objects of Chemistry, its facts admit of explanation, in a form to be intelligible to any educated man. It is not necessary to the progress of this Science, that its language should change with the opinions of every new theorist. The numerical value of atoms and volumes is not of so much importance to a student, as a correct description of the properties and uses of the substances which they represent. On this part of the subject, much labor appears to us to have been wasted by certain writers. They have apparently been engaged in working out an idea, and seeking for some Utopian standard of perfection, in a new system of notation: but in endeavoring to settle contested points on a firmer basis, they have incurred the risk of unsettling everything. Thus, instead of pursuing the inductive method, and fitting hypotheses to facts, they have introduced a deductive system, by which facts are made to bend to hypotheses; and the elementary composition of bodies is altered, in order that they may correspond to certain artificial types. There is an old French proverb which it may be well to bear in mind, in reference to this practice: "*Quand la Nature dit que telle chose est, et l'homme dit que telle chose n'est pas, il faut en croire la Nature.*"

While we do not undervalue the usefulness of a correct language to express the facts and theories of a Science, we have the strongest objection to frequent and capricious changes, in which the good is uncertain and prospective, while the evil is certain and immediate. Chemistry is not the Science of one nation, of one profession, or of one section of chemists. Among civilized nations it has now a community of language, and by this language, it is more closely linked to Arts, Manufactures, and Medicine, than any other branch of knowledge; hence, changes, to be useful, should be such as are required by urgent necessity, and are likely to command general acceptance by their reasonableness and expediency. After all, it must be remembered that these changes are not in the *facts*, but in a supposed improvement in the mode of expressing them; and if only partially adopted, they necessarily lead to confusion. Reasoning from the past to the present, it is not too much to infer that a student of Chemistry must be prepared for a new crop of systematic names, and a new classification of elements and compounds, every ten years.

Our intention in the preparation of this volume has been, not to furnish a Treatise on the Science, but to provide the student, and general reader, with a plain introduction to the subject. With ample materials at our disposal to produce two volumes in place of one, we have studiously endeavored to compress within these pages, a selection of the more important facts and doctrines of Modern Chemistry. We have adopted for the explanation of these facts, that simple chemical language which has found acceptance in the Schools and Colleges of Great Britain, France, and Germany, as well as in the best treatises on the Science.

In addition to the general properties of bodies, we have attached to the description of each substance, a summary of its most important characters, with an account of the special tests required for its detection. The student will thus have in this book a Manual of PRACTICAL CHEMISTRY. As an adjunct to this branch of the Science, the subject of PRACTICAL TOXICOLOGY has been introduced in reference to the most important *poisons*, and the processes for their detection. We have also treated, as fully as our space would permit, the chemical principles on which PHOTOGRAPHY is based, and have given some practical rules for the guidance of those who wish to apply their chemical knowledge to this interesting art.

Having been engaged in teaching Chemistry in this Metropolis, the one for a period of forty, and the other for a period of thirty years, it has appeared to us that, in spite of the number of books already existing, there was room for an additional volume, which should be specially adapted for the use of students. In preparing such a volume for the press, we have endeavored to bear in mind, that a student in the present day has much to learn, and but a short time at his disposal for the acquisition of this learning. An eminent writer has truly observed, that the whole circle of the Sciences is required to comprehend a single particle of matter; but *ars longa, vita brevis.* If a Medical Student has before him only a few years for acquiring a knowledge of at least eight sciences, the efforts of those who contribute to the literature of these sciences should be directed to the elucidation of the most important facts and principles, omitting altogether those details which are either of a controversial nature, or are not yet established on a satisfactory basis. In reference to this book, it may be considered by some, that we have assigned too little, and by others, too much, space to our subject. This, however, is a question of opinion, on which persons may reasonably differ. We have taken that which seemed to us to be the proper course; and we trust we have so dealt with the principles and practice of CHEMISTRY, that the contents of this book will prove useful to the general, as well as to the professional reader.

NOTE.—The limits of this work have not allowed us to occupy our space with a separate essay on PHYSICS. We have, however, described the more important Physical with the Chemical properties of bodies. For further details, we refer the reader either to Peschel's *Elements of Physics*, translated by West, or to the *Elements of Natural Philosophy* of the late Dr. Golding Bird.

We have followed the example of the late Dr. Turner and other writers of repute, in excluding pictorial illustrations. Students of the present day are well acquainted with the shapes of air-pumps, gas-holders, flasks, and retorts. Those who require this aid to their studies, will find in the illustrated catalogues of dealers in Chemicals, more correct representations of apparatus, than those which are commonly met with in treatises on Chemistry.

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CHEMISTRY.

CHAPTER I.

MATTER AND ITS PROPERTIES.

Chemistry as a *science* embraces the whole range of animate and inanimate nature. By its means, man acquires a knowledge of the special properties of bodies, and the laws which govern their combinations. By the application of its principles he can resolve substances into their elementary constituents, and out of old materials construct new compounds. It confers on him a species of creative power, by enabling him to unite elements or compounds, and thus to produce a large number of bodies which have no independent existence in nature. Either directly or indirectly, Chemistry as an *art* lends its aid to the great purposes of civilization. In every civilized country, mining and metallurgy, as well as most branches of manufacturing industry, owe their development and progress to the proper cultivation of Chemistry.

A chemist has to deal with matter, as well as with the forces which are inherent in and connected with it. Matter may be either *simple* or *compound*, and the forces that control it may be either *physical* or *chemical.* Had the globe been constituted of only one kind of substance or matter, the laws of physics alone would have sufficed to explain the phenomena of nature. There are, however, sixty-five different kinds of matter now known to chemists, and as these are resolvable into no other bodies, they are called simple substances or *elements.* But few of these are found in nature in their simple or elementary condition; they are in general intimately combined with each other, constituting the large variety of compounds of which the crust of the earth is composed. These simple substances not only differ in properties, but their compounds also differ as much from each other as from the elements which form them. It is the province of a chemist to define these differences, to determine the laws by which they are brought about, and to establish the relations of this with other branches of science.

Chemistry teaches us that matter is in its nature unalterable and indestructible. It may change its state, and undergo a change in properties, as a result of the chemical force, but it may by the same force be restored to its original state with all its properties unimpaired. Iron and sulphur possess well-marked characters by which they may be easily known from each other; but when combined, as in iron pyrites or bisulphide of iron, these characters are entirely lost, and new properties are acquired. On again separating the two elements, each reassumes its original properties. Chemistry, therefore, is not only a science of properties, but a science of metamorphoses or transformations.

Recent researches have shown that although elements are not resolvable into other substances, they are in some instances so altered by chemical and physical forces, that they apparently lose their identity. We have an example of this metamorphosis of elementary matter, in that condition which is called *allotropy* (αλλος τροπος, change of state), and no substance presents it in so remarkable a degree as phosphorus. Common phosphorus is a waxy-looking solid, melting at or below 111°, and taking fire a little above its melting point. It is dissolved by sulphide of carbon; it is luminous in the dark, evolves an acid vapor in air, and is very poisonous. By exposure to a temperature of 460°, under certain conditions, this substance is so completely changed in its properties that it would no longer be recognized as phosphorus. It presents itself as a hard, brittle, red-colored solid, which may be heated to about 500° before it melts or takes fire, is insoluble in sulphide of carbon, does not evolve any luminous or acid vapors, and has no poisonous action on animals. By the application of chemical reagents and heat, the same products are obtained from it as from common phosphorus; and as no other matter or substance can be extracted from it, and each is convertible into the other, we are compelled to ascribe the difference in properties to molecular changes—a theory which will hardly account for the destruction of the poisonous effects of this element on the animal organism. Oxygen, sulphur, carbon, boron, and silicon, are bodies which may also exist in two or more states in which their properties are widely different. This difference is sometimes brought out by physical, and at other times by chemical agency. These facts show us that the elementary state of matter is not so simple as has been hitherto supposed, and they point to the probability that many of the substances now regarded as elements, may hereafter be proved to be compounds. The allotropic state, however, is not confined to simple substances. Compound bodies, such as silicic acid, and the peroxides of iron and tin, present instances of this condition. The physical and chemical properties of these bodies are changed by heat, or vary with the mode of their production, while their chemical composition remains unaltered.

When two compounds can be proved to be formed of the same elements in the same proportions by weight, it would appear to be a reasonable inference that their properties should be identical; but chemistry teaches us that this condition may exist, and yet the substances be wholly different in chemical and physical properties. Bodies which thus resemble each other in atomic constitution are called *isomeric* (ἴσος equal, and μέρος part), and *isomerism* is the name applied to this condition of matter. The fact is, the properties of the substance depend not only on the nature of the elements, and the number of atoms of each, but on the mode in which these elements are grouped or arranged. Gum, starch, and sugar are isomeric, or are constituted of a like number of atoms of the same elements, and the difference in their properties can therefore only be ascribed to a difference of arrangement among these atoms. Cases of *isomerism* are much more numerous in organic than in mineral chemistry, for the reason that organic compounds are composed of a greater number of atoms of each element, and these admit of a greater variety of arrangement. In some instances, the atoms are in precisely the same number, but the bodies which they form are widely different. Thus, the hydrated cyanate of ammonia is represented by the formula $NH_3,\underbrace{C_2NO}_{},HO$, while the organic compound urea is $C_2N_2O_2H_4$. The properties of these compounds are widely different. That the differences must depend on the arrangement of the atoms is proved by the discovery of Wöhler, that on evaporating a solution of the hydrated cyanate of ammonia this salt disappeared, and the organic principle urea was produced. Oil of turpentine and oil of lemons present another instance of similarity of atomic composition with different properties. Each of these oils contains $C_{20}H_{16}$, but no method is known by which one can be converted into the other. There is a whole group of hydrocarbons similarly constituted. Isomeric bodies in which the atoms are the same in number and relative proportion are called *metameric*, in order to distinguish them from another class called *polymeric*, in which the relative proportions in 100 parts by weight are the same, while the absolute number of atoms differs. Aldehyd and acetic ether are liquids remarkably different in properties, but they are polymeric. Aldehyd is represented by $C_4H_4O_2$, and acetic ether by $C_8H_8O_4$. Two atoms of aldehyd would therefore be equivalent to one of acetic ether; but 100 parts of each liquid would yield precisely the same relative weights of carbon and hydrogen. At the same time these liquids are not mutually convertible into each other. In mineral chemistry, a similar condition presents itself in reference to the compounds known as ferro and ferri-cyanogen. The former is Fe,C_6N_3; the latter has exactly double the number of atoms, $F_2,C_{12}N_6$. In a state of combination, their crystalline forms, color, and chemical properties are wholly different. These facts teach us that the grouping of the atoms, apart from the chemical composition of substances, has a material influence on their chemical and physical properties.

While physics relate to those changes, in masses as well as particles of matter, which result from the physical forces of gravitation, electricity, magnetism, light, and heat, *chemistry* relates to changes produced among the minute particles of bodies which are the result of one peculiar force—namely, *chemical force*, *affinity*, or *attraction*.

Physical Forces.—Physical forces are manifested on the same or on different kinds of matter. The chemical force can be manifested only between different kinds of matter. As a general rule physical forces produce no permanent change in the properties of bodies, while it is the special character of the chemical force, and the leading feature of its existence, that the properties of the bodies on which it has been exerted are permanently altered. *Sulphur* and *iron* will serve to illustrate the differences here indicated. Gravitation affects both, but in different degrees. A cubic inch of iron gravitates with a force equal to that of three and a half cubic inches of sulphur. This is indicated by a comparison of their relative weights in the same volume or bulk (specific gravity). If the mass of iron is rubbed with a flannel, and held near a light substance, such as dry bran, there is no attraction; when brought near to a suspended magnet, each end of the magnet is powerfully attracted; when heated it does not melt; under reflected light it has a gray color and a metallic lustre. A small bar of it held in a flame, allows the heat rapidly to traverse its substance, and it becomes painfully hot, without undergoing any further change. On the other hand, a mass of sulphur warmed and rubbed with dry flannel, powerfully attracts bran and all light substances. Until it has been rubbed it manifests no attraction for the magnet, and after rubbing, it attracts it only as a result of the frictional electricity produced in it; when heated, it readily melts, takes fire, and burns with a blue flame; under reflected light it has a peculiar yellow color without any metallic lustre. Here, then, we have a manifestation of different *physical* properties in these two bodies, and we learn that iron is of greater *specific gravity* than sulphur; that while iron is not rendered *electric* by friction, sulphur becomes highly electric; that while iron is powerfully *magnetic*, there is no magnetism in sulphur; that as to the effect of *heat*, while one is infusible and incombustible at ordinary temperatures, the other readily melts and burns; that the *light* reflected by the two is different, and that while iron allows *heat* to traverse its particles from end to end, sulphur does not. After having manifested all these phenomena as a result of physical forces brought to bear upon them, the iron and the sulphur resume their original state and remain unchanged.

The *chemical* differences which exist between iron and sulphur are not less remarkable. If sulphur in fine powder is sprinkled in a jar inverted in a saucer of water, it may be kept for any length of time without undergoing any change. If iron-filings are sprinkled in another jar, also inverted in water, the iron will be oxidized or rusted, and the water will rise in the jar, showing that a part of its gaseous contents has been removed. The gas thus removed may be proved by experiment to be oxygen, which, at a low temperature, will combine with iron but not with sulphur.

If we mix together iron and sulphur in the finest powder, in the proportions in which we know they will chemically combine to form iron pyrites or bisulphide of iron, namely, forty-seven parts of iron and fifty-three of sulphur, they will remain as a mere mixture, each with its physical properties unaltered. Owing to the presence of iron the powder will have magnetic properties, and when placed in water the iron will rust, and remove oxygen from a vessel of air. If a magnet be drawn over the powder the iron will be removed, and the sulphur remain.

Chemical Force.—When the sulphur and iron are, however, chemically united in the proportions above-mentioned, as in iron pyrites, they will be found to have lost their characteristic physical and chemical properties. This substance is seen in hard cubic crystals of a yellow color and of a metallic lustre. It has no magnetic properties; it is not, like sulphur, rendered electric by slight friction, and in the state of fine powder it does not remove oxygen when placed in a jar of air over water. A magnet drawn over this powder produces no effect upon it, the iron is not separated from the sulphur. We have, in fact, an entire change of properties, and the new properties acquired are retained so long as the two elements are chemically combined. By aid of the chemical force, the two elements may be separated and procured in a pure state. The iron and sulphur will then be found to have re-acquired all the properties, physical and chemical, which they had lost as the result of their combination.

Physical forces, therefore, produce only temporary changes in bodies, while the chemical force entirely alters them; and this alteration continues until the union of the elements is dissolved. Further, we learn that the properties of a chemical compound cannot be inferred from the properties of its constituents. Its physical condition as gas, liquid, or solid, and its chemical and physiological characters, can be determined only be experiment. Nitrogen and hydrogen are two comparatively inert gases, while carbon is an innoxious solid. The combination of these three elements produces a highly poisonous liquid, Prussic acid. Hydrogen has no smell, and sulphur only a slight smell on friction; when combined these bodies produce a most offensively-smelling gas, sulphide of hydrogen. Carbon, oxygen, hydrogen, and nitrogen, are innoxious agents, and have no taste, but when combined in certain proportions they form strychnia, remarkable for its intensely bitter taste and highly poisonous properties. Iron manifests magnetism most powerfully, and oxygen is the most magnetic of gases, yet these two bodies, when combined in the proportions of two of iron to three of oxygen, produce a compound in which no trace of magnetism can be discovered.

The properties of substances which are referable to the senses in the form of taste, odor, color, or touch, are called by the French *organoleptic*, to distinguish them from physical and chemical properties. They are of some importance in chemical analysis, as they often aid the inquirer in his search after minute traces of certain elements or compounds.

Divisibility of Matter.—Matter, in the simple or compound, in the solid or liquid state, is *divisible.* Thus, a solid or liquid may, by various processes, be reduced into particles so fine that they are no longer perceptible to the eye. When reduced to the 1-500,000th of an inch in diameter, the particle would be no longer visible under the most powerful microscope (Mitscherlich); but lines closer together than the 100,000th of an inch admit of no separation by the most powerful modern object-glass. The minute particles of fine precipitates, such as sulphate of baryta or chloride of silver, are individually imperceptible: they are only rendered visible to the eye by aggregation. So of all solids in solution, the particles are so small that light traverses them. A small quantity of mercury shaken in a bottle with strong sulphuric acid, is temporarily split into myriads of minute globules. Mere pressure with the finger will divide this liquid into particles so small that they become gray and their bright lustre is lost to the eye. By subliming the metal in a tube, its particles may be so subdivided as to present only a gray tarnish on the glass. If a solution of chloride of tin is added to a solution of corrosive sublimate, a grayish-black precipitate is formed, which, when separated by filtration, appears on the filter in the form of microscopical globules, so minute that it would be difficult to assign a weight and size to each. Platinum, in the form of ammonio-chloride, is converted by sulphuric acid and zinc into a black powder (platinum-black) resembling charcoal. All the physical characters of a metallic substance are lost by reason of the extreme tenuity of its particles. Gold admits of still finer subdivision. It has been reduced to such a state of tenuity that it does not sink in water, but allows light to traverse it as well as the liquid: its particles giving to the liquid a blue, green, or ruby color, according to the degree to which they have been divided by chemical agency. According to Faraday's experiments, the ruby liquids present metallic gold in the finest state of division; the blue liquids hold the gold in a more aggregated form. That they are finely diffused particles of the *metal* is proved by throwing a cone of sun-rays, either by a lens or mirror, into the midst of the liquid, when the illuminated cone clearly proves them to be undissolved bodies. He estimated that a particle in this state formed 1-500,000th part of the volume of the fluid (*Proc. Roy. Soc.*, vol. 8, No. 24, p. 361). Muncke has calculated, from the diffusion of a known weight of gold over silver wire, that one grain admits of subdivision into ninety-five thousand millions of visible parts, *i. e.* visible under a microscope magnifying 1000 times.—(*Handb. der Naturlehre*, 43.) Films of gold, finer than the finest leaves of the metal, may be obtained by the following process. Place a thin slice of phosphorus on a surface of a very diluted solution of chloride of gold. Cover the vessel so as to prevent the access of light. In the course of twenty-four hours the gold will be reduced to the metallic state, for a considerable extent around the phosphorus. It will present the brilliant colors of the metal by reflected, but will appear bluish-green by transmitted light. The metallic film may be raised from the surface of the solution, by bringing into contact with it a clean surface of glass. It will adhere to, and may be dried and preserved upon the glass. Its tenuity is such, that by mere appearance it is scarcely possible to determine on which side of the glass it is deposited. It is probably less than the millionth of an inch in thickness.

The divisibility of matter is of interest to the chemist, inasmuch as it enables him to speculate on the limits of chemical tests for the detection of substances. If half a grain of nitrate of silver is dissolved and diffused in 100 ounces of distilled water, the presence of the metallic silver throughout will be indicated by the liquid being rendered opaque, from the production of chloride of silver, by the addition of a few drops of a solution of common salt. One grain of silver may here be proved to be split into 138,000 parts. But Malaguti found in sea-water taken off the French coast, that silver was dissolved in it as a chloride, in the proportion of one grain in 100,000,000 grains, so that each grain of water would contain only the 100,000,000th of a grain of metallic silver. No analysis could reveal its presence, except by an operation on a large quantity. (*Quart. Journ. of Chem. Soc.* 1851, vol. 3, p. 69.) One quarter of a grain of acetate of lead dissolved and diffused in 100 ounces of water, will form a solution which is turned of a brown color by sulphuretted hydrogen, in parts as well as in the mass. The lead is here converted into sulphide; and a grain of the metal is actually split into 336,000 parts. With indigo the divisibility may be carried still further. One-eighth of a grain of indigo dissolved in sulphuric acid will give a well-marked blue color to 300 ounces of water. This is in about the proportion of a millionth part of a grain in every drop of water. Muncke, who has ingeniously calculated the *weight* of the minutest visible particle of gold obtainable from the division of a grain of metal, has endeavored, in reference to indigo, to determine the *size* of the minutest particles of this substance from the dilution of a measured quantity of its solution. He estimates it at the five hundred billionth of a cubic inch. (*Op. cit.*, p. 44.)

The divisibility of matter has of late acquired an additional interest in a chemical point of view, by reason of the discoveries of Kirchoff and Bunsen, in reference to the diffusion of metals. Their researches tend to show that sodium, probably in the form of chloride, is a constituent of the atmosphere, and is diffused as a vapor over the whole of the globe. The divisibility of sodium to the extent in which it may be detected by prismatic analysis, utterly defies the balance and the microscope. They have tested the diffusion of the vapor of sodium from a minute quantity by weight in a room of known capacity, and they have detected its presence by the prism when the quantity examined could not have exceeded the 195,000,000th part of a grain in weight.—(*Phil. Mag.*, Aug. 1860, p. 95.) In reference to this mode of analysis they have also announced the presence of a metal (cæsium) in a mineral water, of which it could not have formed more than the 100,000,000th part.

These results and calculations naturally suggest the question, whether there can be any limit to the divisibility of matter. Without going into the metaphysical part of this question, we may state that as bodies in masses can be proved to combine in definite weights, or weights which are fixed for each substance, it is probable that the same is true of the minutest particles of which they are composed. The view most consistent with chemical facts and theories is, that there is a limit to the divisibility of matter, and to this limit the term *atom* (ἄτομος, undivided) is applied. It is believed that at this point matter is no longer divisible. What that limit is cannot be defined, and it is unnecessary for practical purposes to inquire. We can neither calculate nor estimate the size, shape, or absolute weight of atoms, but we can say that they are infinitely smaller than any particles which we can weigh in the most delicate balance, or measure in the field of the most powerful microscope.

Cohesion.—The minute atoms of matter are held together by two forces; first, the force of *cohesion;* and second, the force of *affinity*, or the chemical force. In simple substances cohesion only is exerted. Thus, in sulphur as a solid, and in bromine as a liquid, the particles of each element are held together by cohesion. In compound bodies the two forces are in operation. In a mass of lime the particles are united by *cohesion;* but the oxygen and calcium of which the lime is constituted, are held together by *affiniy.*

The force of cohesion in bodies may be destroyed by physical causes, and the three states in which matter exists, solid liquid, and gaseous, depend on the relative amount of cohesive force exerted among the particles. In a solid the cohesive force is strong, in a liquid it is comparatively slight, and in a gas it ceases to manifest itself. The cohesion of solids is destroyed by pulverization, but more completely by heat, which operates as an antagonistic power. Thus many solids are reduced to a liquid, and ultimately to a gaseous or vaporous state, by the mere effect of heat. Ice, water, and steam, present familiar examples of these states of matter, in the well-known compound of oxygen and hydrogen. We can see a mass of ice or liquid water, but no eye, even aided by the microscope, can see the particles of aqueous vapor into which water is converted above 212°. Some bodies are known only in the solid state, *e. g.*, lime and carbon; others only in the gaseous state, *e. g.*, oxygen; others, again, only in the liquid and gaseous states, *e. g.*, alcohol. From recent experiments, there is reason to believe that bodies hitherto supposed to be of a fixed nature, such as platinum, iron, and even carbon, are capable of assuming the gaseous or vaporous state under the intense heat of the voltaic battery; and that their particles may be thus transferred from one pole to another.

The destruction of cohesion in compounds, whether brought about by mechanical division or by the effect of heat, does not, as a general rule, destroy the chemical force by which the atoms are bound together. Calomel may be reduced to the finest state of powder, or even converted into vapor, by heat; but each atom of the compound still consists of chlorine and mercury. In the same manner the invisible particles which constitute aqueous vapor, contain, in their most extreme division, oxygen and hydrogen. In some instances, heat applied to solids or liquids, either directly or as a result of friction or percussion, will dissever atoms united by chemical affinity. Such effects are seen in the solid iodide and in the liquid chloride of nitrogen; but this is the result, not of mechanical division, but of the decomposing agency of heat on such bodies, brought out by friction or percussion. The atoms of substances which are once chemically combined, require, as a rule, the chemical force for their separation.

Adhesion.—Cohesion may take place between substances of different kinds, but this is by contact of *surfaces*, and is sometimes called *adhesion*. An amalgam of tin and mercury (used in silvering mirrors) adheres closely to a surface of polished glass. The film of reduced metal in the collodio-iodide of silver, on which a photographic image has been produced, adheres very firmly to the glass. Lastly, one metal, platinum, by reason of its expansion and contraction, when exposed to heat, not differing materially from that of glass, may actually be welded to this substance, and on cooling it firmly coheres to it. Stout platinum wire thus welded into short glass rods, forms a useful piece of apparatus for the detection of small quantities of bases by combustion.

Capillary Attraction.—Closely allied to cohesion is that mutual attraction between the surfaces of solids and liquids which gives rise to the phenomena of *capillary attraction*, so called from its causing the visible rise of fluids in tubes of small bore. If a tube with a capillary bore of one-fiftieth of an inch be dipped at one end into a glass of colored water, the water rises to about $2\frac{1}{2}$ inches, and the rise is great in proportion to the smallness of the bore, and is greater with water than with any other liquid. If two plates of perfectly clean glass be so held as to form a very acute angle with each other, and their lower edges be then dipped into water colored by sulphate of indigo, the liquid will rise in the form of a curve (hyperbola) between the plates, rising highest where the space between them is least. It is in consequence of this species of attraction that a drop of water upon a solid surface wets and adheres to it; and that the surface of water in a clean tumbler is not truly level, but a little elevated upon the edges. These phenomena depend upon the nature of the substances presented to each other: thus water will not rise upon greasy glass, or wax; and hence also different liquids rise to different heights in the same tube, independently of their specific gravities, and of their relative degrees of viscidity. Mercury not only does not rise, but is depressed in the bore of a common glass tube: so that, unlike water, it presents a convex instead of a concave surface when contained in a glass tube or vessel, provided the tube or vessel is clean and the mercury is absolutely pure. The cohesive attraction of the particles of mercury to each other is greater than of the mercury to the glass: hence they are incapable of wetting it. This renders mercury well fitted for thermometers of a minute capillary bore.

The rising of liquids in porous or spongy bodies, the ascent of oil or spirit in the wicks of lamps, in which the fibres of cotton or asbestos, by reason of their contiguity, build up small tubes or channels—and the circulation of the juices of plants, are dependent on capillary attraction. If a lump of white sugar is placed on a few drops of diluted sulphate of indigo, the liquid rises and colors the whole substance of the sugar. A heap of dry sand placed in contact with water soon becomes damp throughout. If a short piece of cane is plunged into oil of turpentine, the liquid after a time rises through the fibrous or tubular structure of the cane, and may be burnt as with a wick at the top. A curious instance of capillary attraction operating with crystallization, is furnished by the following experiment: Let a Florence flask be half filled with a saturated solution of bisulphate of potash. Plunge into the liquid a piece of clean white deal stick, so that the end may project one or two inches above the neck of the flask. If kept in a warm and dry place, the liquid will rise by capillary attraction, and a dense crop of prismatic crystals will after some time be formed on the top of the wood. As the small prisms build up tubes, the liquid is gradually drawn through them, and more crystals are deposited, until they fall off as a result of their weight.

The effect of capillary attraction is often seen in crystallizing solutions. The fine prisms deposited at the edge of a vessel where the solution is in contact with it, draw up more of the crystallizing liquid and another crop is formed, in a ring or circle above the liquid. These carry the liquid by capillary attraction still further, so that they sometimes creep up the inside of a vessel and descend on the outside. A prismatic crystallization of carbonate of soda, nitrate of potash, and sulphate of soda, is often seen on walls, covering a large surface, as a result of capillary attraction.

This force is remarkable in the fact that, like cohesion, it is more powerful than gravity. Water and other liquids are lifted perpendicularly in spite of gravitation. It affects the freezing point of water, which is much lower than 32° when the liquid is contained in a capillary tube.

CHAPTER II.

CRYSTALLIZATION—DIMORPHISM—ISOMORPHISM.

THE process by which the cohesive force operates to produce a symmetrical or regular form in bodies is called *crystallization.* A *crystal* (κρύσταλλος, ice or crystal) is a polyhedral or many-sided solid, having smooth and bright surfaces called planes, terminated by sharp edges or angles. This force is chiefly witnessed in bodies as they are passing from the gaseous or liquid to the solid state. The study of this subject is of some interest in reference to analysis. As a peculiar crystalline form is observed in a large number of mineral and organic compounds, an analyst, when assisted by the microscope, is enabled to detect many substances in quantities too small, or in mixtures too complex, for the application of ordinary tests. Thus a crystal of white arsenic not larger than a 20,000th part of an inch may be easily identified.

This force appears to be impressed on the minute atoms of all kinds of matter. Simple and compound, solid, liquid, and gaseous bodies, all more or less assume a crystalline form when placed in the conditions necessary to the process. It appears to be as closely associated with the matter as the force of gravitation itself. Salts not found in nature, but purely productions of art, acquire crystallizing power in fixed and definite forms, whenever the union of their atoms takes place in certain chemical proportions. Thus potassium, iron, carbon, and nitrogen, when artificially combined produce salts which, in one state, form splendid yellow octahedral crystals with a square base (ferrocyanide of potassium); and in another state, right rhombic prisms of a rich ruby color (ferricyanide of potassium), the two compounds differing but slightly in the proportions of one of their component parts.

The *forms* of crystals are generally characteristic of the substance: thus, among native or natural crystals, quartz is known by its transparent six-sided prisms, fluor-spar by its cubes, and Iceland spar by its rhombs. Among artificial crystals, nitre is known by its long fluted prisms, common salt by its cubes, and alum by its well-marked octahedra. Some bodies, such as gum, starch, and glass, cannot be made to assume the crystalline state: they are for this reason called *amorphous,* from α, priv. and μορφὴ, form). Others, like sulphur, assume it most readily, provided cohesion be destroyed by *fusion, sublimation,* or *solution.*

Some bodies, *e.g.*, the metals, can be readily crystallized by fusion; others, as nitre, alum, and the greater number of salts, only by solution; and others, again, *e.g.*, calomel only by sublimation. Corrosive sublimate and white arsenic may be obtained perfectly crystallized either by sublimation or solution, and in reference to arsenic the octahedral form is preserved in both cases. Hence it follows that if a substance cannot be melted, dissolved, or sublimed, it will not admit of crystallization.

Crystallization by Fusion.—If a quantity of pure bismuth is melted in an iron ladle, and is allowed to cool until a slight crust is formed on the surface, and two holes are then made in this crust to permit the still liquid metal to be poured out, a fine group of cubic crystals of bismuth will be obtained. Sulphur melted in a crucible at a low temperature, and treated by a similar process, will yield a hollow cavity containing numerous prismatic crystals, intersecting each other in all directions. The crystals thus obtained will be large in proportion to the quantity of bismuth and sulphur melted, and the slowness with which the cooling has taken place. The melted substances should be kept at perfect rest. Groups of crystals thus procured somewhat resemble the hollow minerals found in different strata called *geodes* (γεώδης, earthy). They are rough-looking globular masses on the exterior, but when broken are found to be lined with crystals of quartz, fluor, and other mineral compounds.

Advantage is taken in the arts of this tendency of certain metals to crystallize by fusion, to separate silver from commercial lead. About six tons of lead are melted at once. In the act of cooling the lead crystallizes in octahedra, and is removed from the molten mass by means of a perforated iron ladle. The melted portion is thereby reduced to about seven hundredweight; and this consists of a very fusible alloy of lead and silver, in which the silver is in large proportion, and can be easily separated from the lead by other processes. The efficiency of this method of separation may be judged of by the fact that the average quantity of silver contained in lead is ten ounces to the ton; and by the crystallization of the lead, the proportion of silver is brought up to two hundred ounces to the ton.

Structure of Crystalline Solids.—The crystallization of sulphur, bismuth, and other metals by fusion, shows that crystallizable bodies are made up of groups of minute crystals, since but for the pouring off of the liquid portion of bismuth or sulphur, the whole would have set into a confused mass. An experiment on tin will further illustrate this condition. If a piece of tinplate (tinned-iron) is warmed, and the surface is then brushed over with a liquid consisting of one part of nitric and one part of hydrochloric acid, with eight parts of water, a very beautiful crystalline structure will be at once made apparent. This has been called the *moirée* of tin. The tin in cooling on the surface of the sheet-iron, assumed a crystalline structure, but this was concealed by a deposit of amorphous metal which the diluted acid removes. Spurious tin-foil, *i. e.*, sheet-lead faced with tin, does not present this crystalline character. When treated with the mixed acids, after a short interval a dark blue or leaden color appears, and the spurious metal is partially dissolved. Most metals by exposure to solvents are found to present a crystalline structure. Platinum thus presents a crystalline surface from the action of nitro-hydrochloric acid, and aluminum may be easily *moirêed* by the action of a solution of potash or soda. Wrought iron immersed in a weak acid solution of chloride of platinum, presents a fibrous structure; and the damasking of steel is produced by washing the metallic surface with diluted nitric acid.

Many salts which are soluble in water, may be made to present a well-marked crystalline structure as a result of partial solution. A rough block of alum placed for a few days in a cold and nearly saturated solution of this salt, will present upon its surface the planes and angles of numerous octahedra. A crystalline structure is also thus brought out on a mass of bichromate of potash, sulphate of iron, or carbonate of soda. The cohesive force which holds together the atoms of salt, appears to be stronger in the planes and angles of the crystal than in other directions; hence these parts resist solution, and the block is unequally dissolved. Ice may be made to present a crystalline structure by soaking a block in water at about 32°. This structure, however, is rendered more apparent by the freezing of thin films of vapor deposited on glass during winter. The same phenomenon is observed with respect to most solids which can be dissolved or sublimed. Thus a rough block of camphor kept in a capacious bottle for some weeks, diminishes in bulk by reason of a portion being volatilized and deposited in crystals in the upper part of the bottle, which has been exposed to light. If the surface of the camphor be now examined with a lens, it will be found to be composed of the planes and angles of well-defined rhombohedra, as if it had been artificially carved.

Cleavage.—To the crystalline structure may be referred the property of cleavage, whereby crystals can be easily broken only in certain directions, corresponding to the planes of crystallization. Masses of selenite (sulphate of lime), Iceland spar, and galena, when struck, will break readily in sharp angular fragments of different shapes, but presenting bright surfaces. When these broken surfaces are examined, they are found to correspond to the planes or layers of the primary form of the crystal, to which each substance may ultimately be reduced by cleavage. Thus selenite readily splits in two directions, and in one of these so easily that it may be reduced to the thinnest plates. By fracture in another direction, the pieces break in the angles of a rhomb, so as to form rhombic plates. Iceland spar (carbonate of lime) on the other hand, may be readily cleaved in three directions, so as to produce a rhomboidal crystal. To this form, the numerous varieties of carbonate of lime may be finally reduced by cleavage. Galena, or sulphide of lead, is met with crystallized as a cube, octahedron, or rhombic dodecahedron. The cubic galena admits of cleavage in three directions, corresponding to the rectangular form of the cube. If an attempt be made to split the octahedral or dodecahedral crystal parallel to the planes of those figures, the crystal will resist the force in these directions, but it may be readily broken in planes parallel to the cube. These three figures have therefore a direct relation to each other: they may pass and repass into each other, and they constitute one of the systems in which crystalline forms are arranged. This property of cleavage shows that the force of cohesion in crystals is stronger in certain directions than it is in others. An amorphous or uncrystalline solid, like chalk or starch, when struck, will break in any direction with a dull and uneven fracture. Another curious fact which was discovered by Mitscherlich is, that a great number of crystals, when heated, expand unequally, *i. e.*, more in certain directions than in others. As a general rule, solids, when heated, expand equally in all directions. The crystals belonging to the cubic or regular system (alum, common salt, white arsenic), also follow this rule; while in the five other systems of crystallization, the crystals, when heated, expand unequally in one or more directions. Thus a rhomb of carbonate of lime, when heated only from 32° to 212°, undergoes an alteration of shape. The obtuse angles become more acute, and there is by measurement a difference of 8½ degrees in the inclination of the planes of the crystal. This can only be ascribed to an inequality in the cohesive force in two opposite directions. On cooling, the crystal resumes its original shape.

Crystallizing Force.—The force with which cohesion is exerted in crystallization is very great. In the crystallization of water during freezing, lead, iron, and glass vessels are burst. This is owing to the increase of bulk which takes place when water passes into ice. (*See* WATER.) The effects of freezing water on rocks, earth, and porous stones are well known. Crystallizing solutions, by penetrating into small cracks or fissures in the vessels which contain them, often cause their destruction. An alloy of eight parts of bismuth, four of tin, and five of lead (fusible metal), crystallizes on cooling from a state of fusion. It expands so as to fill a mould completely, and thus allows a perfect impression to be taken. For this reason, in the act of crystallizing it sometimes causes the fracture of a glass vessel in which it is melted. Cast iron crystallizes on cooling, and expands to such a degree that very accurate impressions may be taken from moulds. The Berlin iron used for this purpose contains phosphorus, which increases the fusibility of the metal, and castings are obtained from this in imitation of the finest filigree work.

Production of Crystals.—It follows from what has been stated regarding the conditions for crystallization, that substances which are insoluble, infusible, or fixed at a high temperature, cannot be crystallized by artificial processes. Carbon, sulphate of baryta, silicic acid, and fluoride of calcium, are found perfectly crystallized in nature, but they do not readily admit of crystallization by art. The natural crystallization of these bodies is probably due to the slow operations of nature over very long periods of time, and to the progressive increase in the size of the crystal by gradual accretion from without.

In employing boracic acid as a solvent for alumina, magnesia, and oxide of iron, M. Ebelmen has succeeded in obtaining octahedral crystals identical in physical and chemical properties with the native spinelle ruby. The substances in proper proportions were fused with boracic acid, and by exposing this mixture for some days to the heat of a porcelain furnace, the solid acid was driven off and hard crystals of spinelle were formed.

When diluted sulphuric acid is added to a solution of nitrate of baryta, the sulphate of baryta, owing to its great insolubility, falls at once in an amorphous powder. It shows no tendency to crystallization. When the same acid is added to a solution of tartrate of potash, a crystalline precipitate (cream of tartar) is slowly separated. This compound is also produced in crystals by suspending by a thread, in the midst of a diluted solution of potash to which a small quantity of alcohol has been added, a large crystal of tartaric acid. One or two drops of a solution of ammonia added to a strong solution of oxalic acid in a watch-glass, will slowly lead to the production of the well-marked prismatic crystallization of oxalate of ammonia. Metallic lead may be obtained in a beautifully crystalline state by immersing a piece of clean granulated zinc in a solution of the acetate of lead, acidulated with acetic acid:—or still better, by the introduction of a piece of clean zinc-foil into a weak solution of nitrate of lead, slightly acidulated with nitric acid. Tin may also be obtained finely crystallized in prisms by placing a piece of granulated zinc in a diluted solution of chloride of tin. When iodide of potassium is added to a solution of nitrate of lead, a rich yellow precipitate (iodide of lead) falls down. This precipitate is amorphous; but if the supernatant liquid is poured off, and the yellow precipitate is boiled for a short time in water, a part of the iodide assumes a crystalline state, appearing under the microscope in triangular or hexahedral plates of a golden color, with shades of green.

By Sublimation.—Among the bodies which are easily obtained crystallized by sublimation, *i. e.*, from a state of vapor, may be mentioned benzoic acid, naphthaline, iodine, white arsenic, and camphor. The last-mentioned substance is slowly sublimed at ordinary temperatures, and if placed in a glass bottle exposed to light, rhombohedral crystals are deposited on the side on which the light falls, showing a remarkable relation of light to crystallization. The following experiments will illustrate this method of producing crystals. Place in a small tube about a quarter of a grain of white arsenic, heat the tube a little above the part where the powder is deposited, then very gradually warm the powder. At about 370° the arsenic will be volatilized, and if not too rapidly heated, well defined and distinct octahedra will be deposited on the cold part of the tube. Place in another tube a few grains of the red iodide of mercury; heat it until it melts, then moderate the heat, and the red powder will be sublimed in splendid rhombic plates of a brilliant yellow color.

By Solution.—We must here select a salt, such as nitre, alum, or sulphate of copper, the solubility of which greatly increases with the temperature. A boiling saturated solution of the salt is made, and the vessel is placed aside, covered over, and kept undistured. The cooling should be allowed to take place very slowly: 100 parts of water at 212° will dissolve 246 parts of nitre, but at 60° this quantity of water will retain only 30 parts of the salt. Hence 216 parts are deposited on cooling in groups of prisms, which are large or small according to the quantity of salt dissolved, and the slowness with which the deposit has taken place. As a general rule, the small crystals are more perfect in form and are more transparent than large crystals. As the crystals of salts are of greater specific gravity than the liquid in which they are formed, they are usually deposited at the bottom of the vessel, or they will adhere to any rough surfaces of wood or string which may be introduced into the crystallizing solution. Under these circumstances they increase in size by the spontaneous evaporation of the solution, and a continued deposit from without, and as they are in the midst of the liquid they retain a perfect form. We have thus seen produced rhombic prisms of carbonate of soda of sixteen inches in length, and stalactitic octahedra of alum of still greater dimensions. If the substance is not very soluble in water (arsenious acid), the crystals are small but perfect, and are slowly produced. If the salt is equally soluble in hot and cold water, no crystals are obtained on cooling the solution. Common salt (chloride of sodium) presents an example of this kind, and by this singular property it admits of separation from a large number of salts. It can only be obtained crystallized from its saturated solution by evaporation (*i. e.*, by the removal of the solvent).

The liquid in which crystals are deposited on cooling, is a saturated solution of salt for the temperature; it is called the mother-liquor. By removing it from the deposited crystals and carrying the evaporation still further, *i. e.*, until a slight pellicle appears on the surface, a fresh crop of the same crystals may be procured, but not so pure as those first obtained. The mother-liquor generally retains the impurities associated with the salt, and thus by repeatedly crystallizing a substance in fresh quantities of water, we may bring it to a state of great purity. In the crystallization of tartar emetic, the arsenic contained in the materials used remains in the mother-liquid; and according to Martius, the larger crystals of tartar emetic which are formed principally in the mother-liquid contain arsenic.—(Gmelin, vol. iv. p. 317.)

The more slowly the evaporation takes place, the larger and finer the crystals. The small and opaque cubic crystals of common salt are obtained by rapid evaporation at a boiling temperature. The large crystals of bay salt are procured by the spontaneous evaporation of brine. A viscid state of the mother-liquor from repeated evaporations, is a bar to the production and deposit of fine crystals. Certain alkaloids and other compounds which do not bear a high temperature are procured perfectly crystallized by allowing the liquids to evaporate *in vacuo* at a low temperature—a vessel of sulphuric acid being placed under the crystallizing liquid, to absorb the aqueous vapor as it is evolved.

Crystals may be made to grow or to increase in size, by selecting those which are perfect—covering them with the mother-liquid, and allowing this liquid to evaporate spontaneously. That the crystals may preserve their regular form while this increase is taking place, it is necessary that they should be occasionally turned, otherwise the deposit will be formed chiefly on the upper parts.

Separation of Salts.—When two or more salts are present in the same solution, if of different degrees of solubility and not isomorphous, they may be separated by crystallization. It is observed that the salt which is least soluble for the temperature is separated first. In the evaporation of sea-water, sulphate of lime, by reason of its insolubility, is first precipitated and removed. Chloride of sodium or common salt is then separated, as this is no more soluble in hot than in cold water, while the other salts associated with it are much more soluble at a boiling than at a low temperature. When the water is exhausted of its crystallizable salts, the residue contains chiefly chloride of magnesium with traces of bromide. It is this chloride which gives an intensely bitter taste to the liquid, hence the residue is called "bittern." When two nearly equally soluble salts are present, that which is in larger quantity is usually separated first.

Deposition of Crystals.—As a general rule all crystals are deposited in the mother-liquor as the solution cools, but there are solutions of certain salts which if kept at rest and so covered as to prevent free access of air or dust, will either not deposit crystals on cooling or deposit them only partially. A hot saturated solution of sulphate of magnesia placed in a vessel secured with bladder may be cooled to 60°, and yet will only partially deposit crystals. On agitating the cooled liquid, more will be deposited. This property is more remarkably manifested by sulphate of soda. This salt when dissolved at a boiling heat in the proportion of two parts by weight of crystals to one part by weight of boiling water, may be placed in flasks or tubes and cooled to 60° or below, without depositing crystals, provided the vessels are kept at rest and the surface of the solution is covered while hot with a stratum of oil, or the mouth of the vessel is firmly secured by caoutchouc or bladder. Upon agitating the liquid, or exposing it to air by cutting through the bladder—by plunging into it a glass-rod or a crystal of the salt, the sulphate immediately begins to crystallize, either from the surface or around the rod or crystal; and the whole speedily forms a crystalline mass. If a quantity of this hot liquid is placed in a tube twelve inches long and is similarly secured, the process of crystallization may be easily watched; the mode in which a solid mass of salt is built up of myriads of prisms intersecting each other in all directions, will be then at once made evident to the eye. We have preserved a solution of this kind, with the process of crystallization thus suspended, for three years, and the ordinary mechanical causes above mentioned brought about crystallization in the whole mass after this long period. From this sudden crystallization of sulphate of soda, we learn that the production of crystals is attended with the evolution of sensible heat, light, and even electricity. The phenomenon is considered to be owing to the fact, that in a hot saturated solution the sulphate of soda is dissolved in an anhydrous state, and so remains on cooling, until slight mechanical causes operate on the solution. Agitation, the introduction of a crystal, or exposure to air, causes the formation of the ten-atom hydrate, so that the water now enters into chemical combination with the sulphate, and the whole sets into a solid mass. There is also a seven-atom hydrate of the sulphate of soda. Transparent crystals of this hydrate are frequently deposited in a flask during the cooling of a saturated solution. They become white on the surface, probably from a loss of water during the formation of the ten-atom hydrate. The crystallization of water itself presents a similar phenomenon. Water kept in a narrow tube and at rest may be cooled to 26°, and yet remain quite liquid. If shaken, or disturbed by the introduction of a small thermometer, a part of the water immediately congeals, and the thermometer rises to 32°.

The liquid employed in the *Storm-glass* presents a remarkable instance of the slight causes which lead to the production and disappearance of crystals in a solution. Two parts of camphor, one part of nitre, and one part of chloride of ammonium are dissolved in a minimum of rectified spirit, to which sufficient water is added to dissolve the two salts, the alcohol being just sufficient to retain the camphor. If the solvents are in too large proportion, the liquid may be brought to the point of saturation by slight exposure to the air. It should be filtered and placed in a long tube. At temperatures between 40° and 70° feathery crystals, chiefly of chloride of ammonium, are produced; but these disappear at the higher temperature. It is supposed that their production is also influenced by electrical changes in the atmosphere; but of this there is no proof whatever. The separation of paraffine from the heavy oil in which it is dissolved, is the effect of a change of temperature. When the oil is cooled to below 40°, the solid paraffine crystallizes, and may be separated by pressure from the liquid.

Interstitial and Combined Water.—Crystals which are deposited in a liquid necessarily retain a portion of the mother-liquor in their interstices. This has been called *interstitial water.* It is removed by draining and drying. The amount contained in any sample of crystals may be determined in the same manner as hygrometric water.—(*See* WATER.)

Many saline substances in crystallizing combine chemically with a certain proportion of water, which is specially defined for each salt. These are *hydrated* salts. Some salts, such as the sulphates of soda and magnesia, form several hydrates—the number of atoms of water with which they combine depending on the temperature at which crystallization takes place. Sulphate of soda may be obtained crystallized in the anhydrous as well as in the hydrated state. The common sulphate contains ten atoms of water. Sulphate of magnesia, crystallized at common temperatures, combines with seven atoms of water. If crystallized by evaporation at a high temperature, there are six equivalents of water: and if crystallized from its solutions below 32°, large crystals containing twelve atoms of water are obtained.—(*Regnault*, 2, 259.) Some crystalline salts contain no combined water; in other words, they are *anhydrous.* The chlorides of sodium and ammonium, and the nitrate and sulphate of potash are instances of this kind. Some of these, when suddenly heated, fly to pieces with a cracking noise, to which the name of *decrepitation* is given. Common salt and sulphate of potash possess this property. On the other hand, alum and phosphate of soda, the sulphates of iron and copper, and the carbonate and sulphate of soda, are hydrated crystalline solids; the combined water in some of them forming more than half the weight of the solid salt. Thus the crystals of sulphate of soda contain 56 per cent. of water, and those of alum nearly 46 per cent. The combined water is driven off by heat, and the salt is dehydrated or rendered anhydrous. If the salt be previously dried, and a given weight of it be then heated in a platinum crucible, the amount of water may be determined. The crystalline form, color, and, to a certain extent, the properties, of the salt are dependent on the presence of this water. The sulphate, phosphate, and carbonate of soda readily lose a portion of their combined water at a moderate heat in a dry atmosphere. The sulphate of soda becomes almost completely dehydrated by exposure; the crystals lose their transparency and fall to a white powder. This spontaneous change in crystals is called *efflorescence:* it is in general characteristic of the salts of soda. It may be prevented by preserving the crystals in a damp atmosphere. On the other hand, some salts, such as the chlorides of calcium and magnesium, the nitrates of lime and magnesia, and the carbonate and acetate of potash, absorb water from the atmosphere, not in definite proportion, but until they are reduced to a concentrated solution of the respective salts. To this property the term *deliquescence* is applied. Many crystals undergo no change in air; they are permanent. This is a character possessed by alum, nitre, acetate of soda, and many other salts, as well as by all native crystals.

The chemically combined water in a crystalline solid does not manifest its presence by dampness or humidity when the substance is powdered. The water, in entering into combination, is in fact solidified in the crystal. Alum is a perfectly dry salt, yet it contains nearly half its weight of combined water. On heating crystals of alum, they readily pass to the liquid condition or melt in their water of crystallization. This is gradually expelled as aqueous vapor by continuing the heat; and a light white porous mass is left, in which no appearance of crystallization can be seen. The residue is *anhydrous* or burnt alum. In this state, and by reason of the loss of its water, the salt acts as a mild caustic. When water is poured over this dry mass the salt recombines with it, and great heat is evolved. Gypsum is the native crystalline state of sulphate of lime: it contains about 21 per cent. of water. When roasted at about 260° this water is expelled, and the crystalline mass falls to a white powder known as plaster of Paris. When this powder is mixed with sufficient water to form a cream, it sets in a few minutes into a firm mass, which by crystallization fills accurately every part of a mould on which it is placed. The setting of plaster of Paris is therefore due to the resumption of the combined water which had been expelled by heat. The strong tendency which sulphate of lime has to unite to water in the act of crystallizing, is well illustrated by mixing together equal parts of diluted sulphuric acid, and a highly concentrated solution of chloride of calcium. When mixed, the liquids set into a solid mass by the water of the two solutions combining with the sulphate of lime produced. When powdered sulphate of copper is heated to a moderate temperature it loses its blue color and forms a white powder. On pouring water over it it becomes intensely hot, the water again enters into combination with the white anhydrous sulphate, and the powder acquires a blue color. The color of the salt therefore appears to depend on the water of hydration. As a further proof of this, the blue crystals become white when placed in strong sulphuric acid, as a result of a removal of the water by the acid. The green crystals of sulphate of iron are also rendered white under similar circumstances.

The influence of the proportion of combined water on the color of crystals is more remarkably seen in the platino-cyanide of magnesium than in any other substance. These crystals are prismatic, and are of a rich red, with reflections of an emerald green color. A strong solution of them imparts to paper a carmine red color, and in this state they contain seven atoms of water. When water is dropped on the red compound on paper it immediately whitens the paper, forming a colorless solution of the salt. By gently heating the red deposit on paper, one atom of water is lost, and the substance becomes yellow; at 212° it loses four atoms of water, and is rendered colorless. If still more strongly heated, it loses all its water and becomes yellow. These facts, as well as the discovery of this salt—the type of a remarkable series—we owe to Mr. Hadow, of King's College. We find that the salt is an admirable test of humidity. If the paper stained with it is rendered yellow or white by a moderate heat, it rapidly resumes its carmine-red color, as a result of hydration either in a damp atmosphere or by merely breathing on it. The chloride of cobalt is another salt which presents changes of color dependent on hydration or dehydration. Paper stained with this solution has a light pinkish-red color; when deprived of water by heat it becomes blue, or, if any iron is mixed with it, green, but it resumes its pink color on cooling.

Freezing Mixtures.—The rapid solution in water, of salts abounding in water of crystallization, is always attended by a diminution of temperature; and the more water of crystallization they contain the greater is their cooling effect during solution. As the water in these salts is solid, their solution cannot take place without at the same time rendering latent a large amount of heat. An ounce of crystals of sulphate of soda mixed with one ounce of water lowers the temperature in consequence of the solid hydrated salt becoming itself liquid; but, as it has been above stated, if an ounce of anhydrous sulphate be employed, the addition of water will raise the temperature, because part of the added water enters into combination with the anhydrous salt, and the latent heat of the water is set free.

Freezing mixtures may be made by causing the rapid liquefaction of the combined water of crystalline salts. If to eight parts of crystallized sulphate of soda we add five parts of strong hydrochloric acid, each being separately at 50°, the acid takes away water from the sulphate, liquefying it at the same time, and it thus renders latent so large an amount of heat as to reduce the thermometer from 50° to 0°. For common purposes, the materials used need not be weighed. The fresh crystals finely powdered should be drenched with strong hydrochloric acid. The acid mixed with ice operates in a precisely similar manner, namely, it causes the rapid liquefaction of the solidified water, and lowers the thermometer from 32° to 17°. Diluted sulphuric acid in the proportion of four parts to five parts of the powdered crystals of sulphate of soda, produces a mixture in which the thermometer sinks from 50° to 3°.

Other curious phenomena are dependent on the setting free of the combined water of crystals. Chloride of ammonium contains no combined water: sulphate of soda contains 56 per cent. These are perfectly dry salts, but when rubbed together in a mortar in equal parts by weight, for some time, they form a liquid mass. In fact, they produce by double decomposition chloride of sodium and sulphate of ammonia. The chloride of sodium takes no combined water, the sulphate of ammonia requires only 18 per cent. Thus 38 per cent. of the water of the sulphate of soda is set free as a liquid, and this causes the liquefaction of the mass. Sulphate of copper and sesquicarbonate of ammonia, when triturated together, form, for the same reason, a semi-liquid mass.

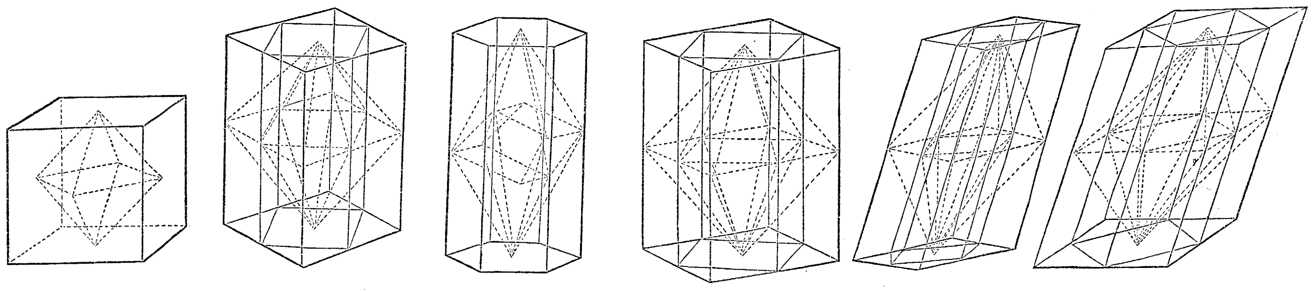
Although it is commonly laid down as a principle that no substances will take on the crystalline state unless they have undergone fusion, sublimation, or solution, there are some exceptions to this rule among the metals. In the process of cementation, iron is converted into steel by heating it with carbon, or, as it is now said, with nitrogen. The iron loses its fibrous and acquires a crystalline character as steel, without fusion. By simple exposure to repeated concussion or vibration, wrought iron is observed to acquire a crystalline structure and to become brittle. This is a change to which the axles of railway carriages are subject, and serious accidents have arisen, from the brittleness of the iron acquired during use, as a result of this crystalline condition. Platinum and silver vessels, frequently heated, undergo, after long use, a similar molecular change, and break with a crystalline fracture. The acquired brittleness of some kinds of brass wire, containing an undue proportion of zinc, may be attributed to a similar cause.

Irregular Forms.—Various names are given to the crystalline structure of bodies when there is an absence of regular form. 1. *Fibrous*, spicular or acicular, crystallization is seen in gypsum and sulphide of antimony. 2. A *laminated* or foliated structure is observed in mica, petalite, and other minerals. 3. The substance may have a *granular* structure still presenting bright but irregular surfaces on fracture. Loaf-sugar, marble, and alabaster are examples of this kind. 4. *Plumose* or feathery crystallization is seen in chloride of ammonium, sulphate of strychnia, and other salts. 5. *Stellated* crystallization is seen in the grouping of minute prisms crossing each other at various angles. Strychnia and many other substances often present themselves in this form.

Regular Forms.—The external forms of regularly crystalline solids are subject to great variation. The nature of the solvent, the temperature, and the presence of other substances in the liquids, modify the form, by creating new planes or angles, so that the true shape of the crystal may be no longer recognizable. The octahedral crystals of alum lose their solid angles when an excess of acid is present, and they become converted to cubes when alumina predominates. In foul and muddy liquids crystals are usually deposited in their simplest forms; in gelatinous and saccharine solutions they are generally single, and remarkably sharp and regular. Common salt deposited from an aqueous solution containing urea, crystallizes in octahedra instead of cubes, which are its usual figure; and sal ammoniac under the same circumstances forms cubes, whereas in pure water its crystals are octahedral. Berzelius states that large crystals of nitre may be obtained from its solution in boiling lime-water, which has no other analogous effect upon other salts. Native crystals of the same substance are met with in great variety. Carbonate of lime is said to present itself in a hundred varieties of form; but these are all reducible to one common figure by cleavage, namely the rhomb. Iron pyrites may be met with either in cubic, octahedral, or dodecahedral crystals; but these are forms which are reconcilable with a systematic arrangement of the molecules around similar axes.

In order to facilitate the study of this subject, and to reduce the large variety of forms to a few well-marked classes, chemists now generally agree in assigning crystals allied in form, to one of six different systems of crystallization, the particles of the substance being supposed to be symmetrically arranged around certain imaginary axes of the crystal. A system, therefore, includes all those forms, however varied, which can be referred to the axes which are peculiar to it. We give on the next page, a table of the special characters of the six systems of crystallization as described by Weiss, including their allied forms and their relations to heat and light.

PHYSICAL CHARACTERS.		SYSTEMS.	ALLIED FORMS.	EXAMPLES.
1 Single Refraction. Expansion equal in all directions		1 CUBIC, OCTAHEDRAL, TESSULAR or REGULAR. 3 rectangular axes, all equal.	1 Cube. 2 Regular Octahedron. 3 Tetrahedron. 4 Rhombic Dodecahedron. 5 Trapezohedron.	Copper, Nickel, Gold, Lead, Alum, Common Salt, Arsenious Acid, Diamond, Fluor Spar, Iron Pyrites, and Garnet.
2 Double Refractions. Expansion not equal in all directions.	One axis of no double refraction. Expansion equal in 2 directions at least.	2 RIGHT SQUARE PRISMATIC. 3 rectangular axes, 2 equal.	6 Square Prism. 7 Octahedron with a square base.	Ferrocyanide of Potassium, Cyanide of Mercury, Calomel, Tin.
		3 RHOMBOHEDRAL. 3 equal axes not rectangular, intersecting at 60° 1 perpendicular to the three.	8 Rhombohedron. 9 Bipyramidal Dodecahedron. 10 Hexahedral Prism.	Calcareous Spar, Nitrate of Soda, Ice, Camphor, Tourmaline, Quartz, Amethyst, Emerald, Corundum, and Graphite.
	Two axes of no double refraction	4 RIGHT RECTANGULAR or RHOMBIC PRISMATIC. 3 rectangular axes, no two equal.	11 Right Rectangular Prism. 12 ——Rhombic Ditto. 13 ——Rectangular Octahedron. 14 ——Rhombic Ditto.	Sulphur, Nitre, Rochelle Salt, Topaz, Arragonite, Bichromate of Potash, Citric Acid, Sulphates of Magnesia, Baryta, Potassa, and Zinc.
		5 OBLIQUE RECTANGULAR or RHOMBIC PRISMATIC. 2 axes oblique, the third perpendicular to both.	15 Oblique Rectangular Prism. 16 ——Rhombic Ditto. 17 ——Rectangular Octahedron. 18 ——Rhombic Ditto.	Felspar, Mica, Epidote, Sulphate and Carbonate of Soda, Chlorate of Potassa, Borax, Sugar, Sulphur, Sulphate of Lime, and Oxalic Acid.
	Expansion unequal in 3 directions.	6 DOUBLY-OBLIQUE PRISMATIC. 3 axes, all intersecting each other obliquely.	19 Doubly-oblique Prism. 20 —— Octahedron.	Sulphates of Copper and Iron, Sulphate of Cinchonia, and Nitrate of Bismuth.


1 2 3 4 5 6

The above engravings represent the six crystalline systems, with their principal derivative forms and planes of cleavage.

[To the reader who wishes to pursue this subject, we recommend the small and concise "Précis de Cristallographie" of M. Laurent. Models in white wood, representing the systems of crystallization and the principal allied forms, may be obtained of dealers in chemical apparatus.]

The student should make himself acquainted with the common external forms of well-known substances, including the cube, octahedron, and its derivative, the tetrahedron—the square, hexahedral, oblique, and rhombic prisms, and plates. A few drops of a solution of the substance in water or alcohol, left to spontaneous evaporation on a glass slide, will furnish a group of crystals, of which the forms can be well determined by a low power of the microscope. If we have to deal with a soluble solid in fine powder, we should dissolve a quarter of a grain in a few drops of water or alcohol on a glass slide, according to the solubility of the substance in either liquid. The liquid should be warmed, until its circumference acquires a slight but visible margin of saline matter. The glass may then be placed aside, and the liquid allowed to crystallize slowly. No crystals are so perfect for microscopical observation as those which are procured in dry and warm weather by spontaneous evaporation. This micro-chemical examination will not only guide analysis by leading to an immediate suspicion of the real nature of the substance—but it will enable a chemist to detect and pronounce an opinion on the impurities in the substance examined; and in medical practice it may suggest the nature of the disease, and point to a plan for treatment. The sedimentary deposits in urine are now easily recognized by their crystalline forms, and the presence of urea, uric acid, or cholesterine in the blood or other liquids, is known by the peculiar crystalline shape which each assumes.

Dimorphism (δὶς and μορφὴ, two forms).—It is a remarkable fact that the same substance may present itself in crystalline forms belonging to two different systems: such bodies are called *dimorphous*. This is the case with *sulphur*, which when crystallized by fusion yields oblique rhombic prisms (5th system), but is deposited from certain of its solutions in octahedra with a rhombic base (4th system). Carbon, in the form of diamond, crystallizes in octahedra, but as graphite, in hexagonal plates. Carbonate of lime in calcareous spar has the rhombohedral structure, but in arragonite that of the rectangular prism; and there are other analogous instances. It has been found in regard to these cases of dimorphism, that each form has its peculiar density; the specific gravity of calcareous spar, for instance, being 2·71; that of arragonite is 2·94. The temperature too at which the crystals are formed is another influencing cause: thus when carbonate of lime is precipitated by adding chloride of calcium to carbonate of ammonia, the grains of the powder are rhombohedral if thrown down at the temperature of 50°, but octahedral if at 150°. (G. Rose, *Phil. Mag.*, xiii. 465.)

The iodide of mercury presents a remarkable instance of dimorphism. It is of a rich scarlet color, and as it is obtained crystallized from a saturated solution in iodide of potassium, it assumes the form of octahedra, with a square base. When heated it becomes yellow, forms an amber-colored liquid, and may be sublimed in rhombic plates of a rich yellow color. In twenty-four hours these crystals, either partially or wholly, acquire a scarlet color. Mr. Warington has observed the rhombic plates to break into octahedra with a square base, as they changed from yellow to scarlet. Hence it is reasonable to infer that there is a spontaneous change in the molecular condition of this salt; indicated not merely by change of form but by change of color in the crystal. The scarlet powder may be crystallized on a card without fusion, by heating it over a spirit-lamp (thus furnishing an instance of the crystallization of solids): and if, when cold, the yellow crystalline compound is rubbed with a piece of paper, it is re-converted to the red iodide. These differently colored crystalline forms may be regarded as allotropic states of the substance.

Dimorphous bodies, or substances crystallizing in the incompatible forms of two different systems, must be regarded as exceptional to the general law of crystallization. It is a curious fact, however, that when this condition exists, the substance frequently presents in its two forms marked differences in hardness, specific gravity, lustre, solubility, fusibility, optical characters, &c., thus showing a molecular difference throughout. In addition to the substances above mentioned, dimorphism has been observed in specular iron ore, iron pyrites, the carbonates of iron and lead, arsenious acid, oxide of antimony, the sulphates of magnesia, zinc, and nickel, and in the seleniates of the two latter metals. It has been noticed with respect to some of these cases of dimorphism, that the crystal of one system is made up of groups of crystals of the other system. The sulphate of nickel crystallizes in right rhombic prisms. Mitscherlich found that when these prisms were heated and broken up, they were resolved into minute crystals of the second system, namely, octahedra with a square base. The crystals of sulphur, recently obtained by fusion, are in the form of oblique rhombic prisms of a yellow color, transparent and somewhat flexible. In a few days they become opaque and brittle, and they fall to a powder which, under the microscope, is found to consist of rhombic octahedra.

Isomorphism (from ἴσος similar, and μορφὴ form.)—Although substances may in general be identified by their special forms, yet different substances, like white arsenic and alum, may present themselves in similar forms. Sometimes a similarity of form is presented by substances which also resemble each other in atomic constitution, or in the number of atoms of acid, base, or water, which enters into their composition. In this case it has been found that such bodies may replace each other, or be substituted for each other in combination, without affecting the crystalline form. Thus the arseniate and binarseniate of soda have the same forms as the phosphate and biphosphate of soda; and the arseniate and binarseniate of ammonia resemble the phosphate and biphosphate of that alkali. Such salts are termed *isomorphous.* In the above instances, the equivalents of acid, base, and water of crystallization correspond; and a similar correspondence has been traced in the atomic constitution of the acids and bases of the salts. Thus the arsenic and phosphoric acids each include one equivalent of base and five of oxygen, and are therefore themselves isomorphous; so also phosphorus and arsenic are presumed to be isomorphous—isomorphous compounds, in general, appearing to arise from isomorphous elements. They have the same garlic odor in the state of vapor, and combine with the same number of atoms of hydrogen to form gases. So also in respect to the isomorphism of the sulphates, seleniates, chromates, and manganates of the same base, each of the *acids* in these cases contains three atoms of oxygen to one of the metalloid or metal. In respect to *bases,* similar analogies are observable; thus the salts formed by magnesia, the protoxides of zinc, iron, nickel, cobalt, and copper, with a common acid, are isomorphous; and alumina and the sesquioxides of chromium, manganese, and iron, each of which contains two atoms of base and three of oxygen, replace each other in many combinations without change of crystalline form. This is seen in the different varieties of alum. The following is a tabular view of some isomorphous groups :—

Chlorine	Chloric acid	ClO_5
Iodine	Iodic acid	IO_5
Bromine	Bromic acid	BrO_5
Sulphur	Sulphuric acid	SO_3
Selenium	Selenic acid	SeO_3
Chromium	Chromic acid	CrO_3
Manganese	Manganic acid	MnO_3

Phosphorus	Phosphoric acid	PO_5
Arsenic	Arsenic acid	AsO_5
Arsenic	Arsenious acid (unusual form)	AsO_3
Antimony	Teroxide of antimony	SbO_3
Barium	Their oxides	BaO
Strontium		SrO
Lead		PbO
Calcium	(in arragonite)	CaO
Potassium	Their oxides	KO
Sodium		NaO
Ammonium		NH_4O
Calcium	Their oxides	CaO
Magnesium		MgO
Manganese		MnO
Iron		FeO
Zinc		ZnO
Cadmium		CdO
Cobalt		CoO
Copper		CuO
Nickel		NiO
Aluminum	Their sesquioxides	Al_2O_3
Manganese		Mn_2O_3
Iron		Fe_2O_3
Chromium		Cr_2O_3

Common alum consists of sulphate of alumina united to sulphate of potash with water of crystallization. It crystallizes in well-marked octahedral crystals. Soda and ammonia are isomorphous with potash, and each may take the place of this alkali without affecting the form of the crystal. So again the oxides of manganese, iron and chromium are isomorphous with the oxide of aluminum (alumina). Each of these oxides may take the place of the alumina, the other constituents remaining the same, and the octahedral form of the compound will be unaltered. A crystal of potassa-alum may therefore receive a deposit of ammonia-alum in a solution of that salt, and it has even been found, as a remarkable instance of the tendency of isomorphous salts to crystallize together, that a white crystal of potassa-alum may be coated with a layer of deep ruby-red chrome-alum; and it is stated that if a solid angle be broken off, chrome-alum may be deposited in its place. From this ready association of isomorphous salts, it is difficult to purify them by crystallization. Thus all commercial alum contains oxide of iron, which replaces part of the alumina. Sulphate of magnesia and sulphate of zinc are isomorphous, and if mixed, they crystallize, more or less, together, so that other means must be resorted to in order to separate them. This observation applies also to the sulphates of copper and iron, which belong to the same system. They are isomorphous in regard to acid and base, and, when mixed, each crystallizes with seven atoms of water. It is a curious fact, that pure sulphate of copper, in crystallizing, combines with only five atoms of water; but if sulphate of iron is present, it will crystallize with seven atoms, like this sulphate. The two are then isomorphous, and they cannot be separated from each other by crystallization. If a large crystal of sulphate of copper is placed in a nearly saturated solution of sulphate of iron, it will be increased in size by a deposit of this salt on the outside, and a crystal may thus be constructed of successive layers of either salt. Although the carbonates of iron and magnesia are isomorphous, the sulphates of these bases are not. They contain different quantities of water of crystallization, and when a solution of the mixed salts is concentrated by evaporation, crystals of each are separately deposited.

Besides a reliance upon form, the measurement of the angles of crystals when of similar form, is sometimes necessary for the purposes of mineralogy. An appropriate and beautiful instrument for this purpose is the *goniometer* of Dr. Wollaston. Its action depends on the reflection of light from the polished surface of a crystal, however minute. By rotating a brass circle, the value of the angle made by any two planes is at once determined; and as a vernier is attached to the scale, a very slight difference in the angles of two similar rhombs may be readily determined, and the identity of each, made out. Thus the carbonates of lime and magnesia assume the rhombohedral form, and are alike in cleavage. By the goniometer, however, it is found that in carbonate of lime the angles formed by the two planes is 105° 5′, while in the rhomb of carbonate of magnesia the angle is 107° 25′. These measurements supply means of identifying these minerals.

CHAPTER III.

CHEMICAL AFFINITY—SOLUTION—ELECTROLYSIS.

Chemical Affinity.—The special characters of the chemical force have been already explained. While cohesive attraction merely unites the atoms of similar or dissimilar kinds of matter without altering their properties, chemical attraction or affinity leads to the union of dissimilar atoms with a more or less complete change of properties.

A chemical compound is known, 1. By the substances uniting in definite proportions by weight—these proportions being called atomic, or equivalent weights. 2. By their union being attended with the absorption or evolution of heat, or the evolution of light, electricity, and magnetism. 3. By a change of properties—thus the density, color, solubility, and crystalline form of the compound, as well as its reactions on other bodies, are in general different from those of its constituents.

This force is only manifested between the minute particles of matter. Place a few grains of powdered iodine in a capacious jar, *i. e.* of 200 *c. i.* capacity. After agitation for a few minutes the particles of iodine will be found diffused through the whole of the jar. They are quite invisible, but in a mass they may give a slight pink tinge to the aërial contents. If a long strip of bibulous paper, soaked in a solution of starch, be now gradually introduced, the presence of the atoms of iodine, and the formation of a chemical compound with the starch, will be indicated by the gradual production of a purple or blue color in the paper. Although five times the weight of water, and four thousand times the weight of the air in which they float, these imponderable atoms clearly indicate their presence and diffusion by a chemical action on starch. If the paper is now removed, and a leaf of silver (made to adhere to a glass-plate by breathing on it), is brought over the mouth of the jar so as to close it, the chemical formation of iodide of silver will be indicated by the production of circular films on the metal, of a straw-yellow, purple, blue, and brown color, each of these films indicating an infinitesimal tenuity of iodide of silver, probably less than the 2,000,000th of an inch in thickness. On a purple film thus obtained, an image may be produced by light in the Daguerreotype process.

Influence of Cohesion.—As a general rule, the more perfectly cohesion is destroyed in substances, the more strongly is chemical affinity manifested. A small block of tin covered with nitric acid in a glass, will show only a slight amount of chemical action. If an equal weight of tin in the state of powder is similarly treated, the acid is decomposed with great violence. So in acting upon equal weights of calcareous spar in lump and fine powder, by adding to them diluted hydrochloric acid, a striking difference will be observed in the relative amount of chemical action. The reduction of a solid to powder operates simply by increasing the surface for chemical action, which, *cæteris paribus*, is always proportioned in intensity to the surfaces of contact between bodies. A cubic inch of a substance exposes only six square inches of surface; but if divided into a million parts, that small area is multiplied into 416 square feet. The finest pulverization of all *solids* is therefore a necessary condition for a perfect and rapid chemical combination.

A stream of sulphuretted hydrogen gas may be allowed to fall on a mass of anhydrous oxide of iron (hæmatite) without producing any chemical changes. If, however, the gas is passed on the anhydrous oxide in fine powder, the whole mass becomes speedily red hot, and water and sulphide of iron are produced. The same gas may be passed into pure water contained in a flint-glass vessel without indicating the presence of lead in the glass; but if the flint-glass finely powdered is thus treated, it is rendered brown by the conversion of the oxide of lead contained in it into sulphide of lead.

Liquids readily combine on mixture; and some gases combine on contact, although in the latter case heat or electricity is generally required to bring about their union. Solution facilitates chemical action by reason of the infinitesimal division to which a solid is thereby reduced; and so frequently is this a preliminary to chemical processes, that the maxim *corpora non agunt nisi soluta* is a generally accepted truth. At the same time in reference to solids which are not easily brought to a state of solution, the operator must equally bear in mind the rule—*corpora non agunt nisi divisa.*

The effect of the minute division of solids in accelerating chemical action is well illustrated in *pyrophori*—substances which are spontaneously combustible on exposure to air. If finely powdered Prussian blue is heated intensely in a glass tube, and then hermetically sealed, the brown-black powder into which it is converted, instantly takes fire, with bright scintillations, on exposure to air. If dry tartrate of lead is heated in a tube to a dull red heat, *i.e.*, sufficient to carbonize the acid (and the tube is hermetically sealed), the residue, when exposed to air, will take fire and burn. In the one case, minute atoms of iron, and in the other of lead, are instantly oxidized with the phenomena of combustion at the ordinary temperature; although neither iron nor lead will burn in air under common circumstances. Sulphate of potassa in powder, strongly heated in a covered crucible, with half of its weight of lamp-black, is converted into sulphide of potassium, which becomes so rapidly oxidized on exposure to air, that it will take fire and burn. The difference between the combustibility of carbon as tinder, and of carbon as coke or diamond, is also dependent on the different cohesive force and amount of surface exposed by the substances. Again, fine zinc shavings are very combustible in the heat of a spirit-lamp, while a bar of the metal, or stout foil, resists combustion. There is no case in which this effect of division and surface is more strongly manifested than in phosphorus. This substance may be exposed to air in a mass, at temperatures below 60°, without taking fire. When dissolved in the sulphide of carbon, and the solution is poured over a sheet of thin paper, a layer, consisting of infinitely minute particles of phosphorus, is left upon the paper by the evaporation of the solvent; and when dry, the fine particles of phosphorus on the covered portion of paper, burst into a sheet of flame. We are accustomed to speak of oxygen as it exists in our atmosphere as passive, but these facts show us that its passivity is more apparent than real; and that were it not for the force of cohesion by which the particles of matter are held together as solids, many of the metals and metalloids could not possibly exist in an unoxidized condition.

In some exceptional cases, solids are found to react upon each other. Potassium placed on ice will decompose it, and burn at the expense of the oxygen, which is one of its constituents. If powdered iodine be placed on a freshly cut slice of dry phosphorus, mere contact leads to the fusion of the phosphorus, and to instantaneous combination with combustion. A mixture of finely powdered chlorate of potash and allotropic phosphorus explodes with the slightest friction and with tremendous violence.

Influence of Water.—The influence of water on chemical affinity is very remarkable. In some cases, by its removal, chemical changes are entirely arrested. Albumen or gelatin, combined with a small quantity of water, speedily putrefies; but when desiccated, or deprived of water, these substances undergo no change.—(*See* WATER.) Iron has a great tendency to become rusted or oxidized on exposure to air; but if the air is perfectly free from water, there is no rusting or oxidation. A strong solution of nitrate of silver dried on paper is decomposed in a few days, even when kept from light. The organic matter of the paper reduces the silver to the metallic state in the dark, and the paper becomes discolored. If, however, the paper is placed in a vessel containing chloride of calcium, and kept from the light, it may be preserved unchanged for weeks and months. Sensitized papers used in the art of photography, or photographic drawings when once taken, are thus effectually preserved from change, so long as they are in a dry atmosphere. Even pure chloride of silver, prepared as white as snow, by immersing leaf-silver in chlorine gas, undergoes no change on exposure to light, provided chloride of calcium is placed in the vessel containing it, and the vessel is accurately closed. We have thus kept the chloride of silver for six months, with its whiteness unaltered, although during that time it was exposed to the direct solar rays. The film of iodide of silver, which is used in the collodion process of photography, may be kept for many months in the dark, with its sensitive powers undiminished, provided the surplus nitrate of silver is removed by washing—the film itself is dried and coated with a layer of albumen or tannic acid, and lime or chloride of calcium is placed in the box to absorb any moisture.

In the absence of water we can get no evidence of *acidity* or *alkalinity* in substances. Thus sulphuric acid in the anhydrous state is a fibrous solid, which has no action on litmus, and no corrosive properties. Solid anhydrous phosphoric acid has no acid reaction on test-paper; this is only manifested on the absorption of some water from the air. Boracic acid and silicic acid are in the same condition; in fact, owing to its entire insolubility in the free state, silicic acid cannot be proved to have any acid reaction at all. Dry carbonic acid gas has no action on dry litmus. The same remark may be made of the gallic, pyrogallic and other vegetable acids, whether hydrated or anhydrous. They manifest no acid reaction on test-paper until water is added. It has been supposed that this apparent production of acidity by water was a proof that all acids must owe their acidity to *hydrogen*, and be really hydracids, hydrides of new radicals, or, as they are termed, "salts of hydrogen;" but such an hypothesis is not necessary for an explanation of the facts. Thus, in reference to the elements of phosphoric, carbonic, pyrogallic, and other acids, water may simply act as a solvent to bring the constituents of the acid in contact with the vegetable color. Anhydrous potassa, soda, ammonia or morphia in the absence of moisture or water, cannot be proved to exert any alkaline reaction on vegetable-colors; and to explain this reaction, it is not necessary to suppose that the potash or soda absorbs another atom of oxygen and becomes a hydride (*see* OXACIDS, and OXYGEN), or to assume therefrom that hydrogen is the cause of alkalinity. Among salts which readily decompose each other, this entire want of action is observed unless water is present. Dry tartaric acid has no action on dry carbonate of soda, even when finely powdered. In the cases above-mentioned, water as such may take a share in promoting chemical action without necessarily undergoing decomposition. (For other instances, *see* WATER.)

In the chemical process of bleaching by chlorine, it is highly probable that water is decomposed. Dry chlorine has no bleaching action on dry vegetable colors. The slightest trace of humidity in the gas or in the colored material brings about the destruction of color. As hydrochloric acid is found in a liquid thus bleached, some portion of the water must have parted with its hydrogen; and oxygen thus liberated in the nascent state (as ozone) enters into combination with the coloring matter and probably operates as the direct bleaching agent.

Influence of Heat.—Heat plays an important part in reference to chemical affinity. By its agency bodies are united and disunited. Mercury combines with oxygen at one temperature, and at a still higher temperature, the compound is again resolved into mercury and oxygen. Protoxide of barium will at one temperature take another equivalent of oxygen, to form peroxide; but when this compound is more strongly heated, the atom of oxygen will be expelled, and it will revert to the state of protoxide. Generally speaking, the effect of heat is to increase the affinity of bodies for each other. Thus sulphur and charcoal have no tendency to combine with oxygen unless heated to about 500° and 1000° respectively, when they both undergo combustion, and produce gaseous compounds. The inflammation of gunpowder furnishes an example of the effect of heat on these ingredients. It is only when this substance is heated in air to a temperature above 500° that combustion takes place, with the conversion of the solid into a large volume of gases.

The solubility of substances in water is generally increased by heat: in some instances, the reverse condition is observed. Lime is twice as soluble in cold as in boiling water; hence when a saturated solution of lime is boiled, a portion of this alkaline earth is deposited. A very diluted solution of persulphate of iron is decomposed by heat, and a basic salt with excess of oxide is deposited. The effect of heat on albumen is remarkable. At a temperature exceeding 170°, the soluble is converted into the insoluble variety, and the properties of the substance are entirely changed. Heat destroys temporarily the combination of iodine with starch; the liquid from being intensely blue becomes colorless; but if not too long heated the color of the liquid will be restored on cooling, by the reabsorption of the vapor of iodine, which has been temporarily separated from the starch. When this experiment is performed in a close vessel the colored compound is reproduced; but when in an open dish, the iodine is lost by volatilization, and the blue color is either not restored, or only in a slight degree. A solution of chloride of calcium, so diluted as to yield no precipitate with a solution of sulphate of soda, undergoes decomposition when heated, and sulphate of lime is precipitated, the salt being less soluble in hot than in cold water. Again, borate of soda produces no precipitation or apparent decomposition of sulphate of magnesia in the cold, but when a solution containing the live salts is boiled, an insoluble borate of magnesia is thrown down. A solution of bicarbonate of soda, or of carbonate of lithia, gives no precipitates with sulphate of magnesia until the liquids have been boiled. It is unnecessary to specify additional instances of the influence of heat on chemical affinity. Illustrations will be found in the history of every element and of most compounds.

Influence of Light.—The influence of light is seen in some combinations of the gases, as well as in the changes produced in the salts of certain metals, as silver, mercury, gold, chromium, iron, and uranium. When equal volumes of chlorine and carbonic oxide are exposed in a glass vessel to solar light, they combine to form a compound known as *phosgene gas.* In the dark they manifest no tendency to unite. When chlorine and hydrogen are mixed and exposed to the direct rays of the sun, they combine with explosion, and produce hydrochloric acid; in the dark there is no combination; and in the diffused light of day the union of the gases takes place slowly, without explosion. So strictly does this union depend on light, that Bunsen and Roscoe have made use of such a mixture for the purposes of photometry, in determining the relative intensity of light. On the other hand, under the influence of light, aqueous vapor mixed with chlorine undergoes decomposition, hydrochloric acid and oxygen being the products (*supra*). Unless a solution of chlorine is carefully kept in the dark, it is rapidly decomposed, and the liquid becomes strongly acid from the hydrochloric acid produced. It is under the influence of solar light that carbonic acid is decomposed by the leaves of growing vegetables, and the carbon is fixed, while oxygen is liberated.

The influence of light on chemical affinity is especially seen in the changes produced on the salts of silver. When in contact with organic matter, nitrate of silver is entirely decomposed by exposure to light. The oxygen and nitric acid are removed and the silver is reduced to the metallic state. If moisture is present, chloride of silver is also decomposed by exposure to light, hydrochloric acid is produced, and metallic silver is deposited. In reference to these salts, the changes are physical as well as chemical—the silver is visibly darkened. Other salts of silver, such as the iodide and bromide, undergo no visible change of color when exposed to light; but they are altered in their molecular state. (See p. 48.) This subject will be more fully considered in the subject of PHOTOGRAPHY. The suboxide of mercury, exposed to light, is converted into red oxide and metallic mercury. Turpeth mineral, or the basic sulphate of the peroxide, is darkened by light. The salts of the peroxide of iron, formed by the citric and oxalic acids in contact with organic matter, are reduced to proto-salts by exposure to light, a fact which may be proved by the application of appropriate reagents, *e. g.* the chloride of gold. The persalts of uranium and the bichromate of potassa are also reduced to lower degrees of oxidation by exposure to the solar rays.

The effects above described take place under the influence of ordinary light; but a closer analysis of the phenomena has established the fact, that this chemical influence is almost exclusively confined to the more refrangible rays of the spectrum, namely, the blue and violet. Thus, an intense light passing through violet or blue glass will cause the immediate explosion of a mixture of chlorine and hydrogen; while the same light, traversing yellow or red glass, has no combining effect on the gases. Although a larger amount of luminosity exists in the yellow than in the blue light, the yellow rays are powerless to bring about a chemical union of the gases. This peculiar effect of colored light is equally observed in reference to the changes produced on the salts of silver; but in different degrees in different salts. The rays which produce these chemical changes are called *actinic;* they are met with even beyond the visible violet ray. On the undulatory theory of light, the blue and the violet rays are considered to produce a greater number of ethereal undulations, in a given time, than the yellow and the red rays; and the difference of color is supposed to depend upon the difference in the number of their undulations. While this theory derives great support from many physical phenomena, it affords no satisfactory explanation of the remarkable influence of white or colored light upon the chemical union and decomposition of bodies.

Influence of the Nascent State.—Gases when once in the free state do not readily combine with each other. Thus hydrogen will not combine with nitrogen to form ammonia, nor will it combine with sulphur or arsenic in powder or vapor, to form sulphuretted or arsenuretted hydrogen; but there is a condition called the *nascent* state, which is eminently favorable to the chemical combination of these bodies, either with each other or with solids. The *nascent* state simply implies that condition in which a body is passing from the solid or liquid to the gaseous state. The ammonia formed by the putrefaction of substances containing nitrogen, is the result of the combination of hydrogen and nitrogen, as they are liberated from the organic solid or liquid. When sulphide of iron is treated with diluted sulphuric acid, the nascent hydrogen resulting from the decomposition of water, instantly seizes upon the sulphur of the sulphide, to form sulphuretted hydrogen. When the same acid is poured upon zinc, containing arsenic, or when the zinc and acid are added to an arsenical liquid, the nascent hydrogen instantly combines with the arsenic to form arsenuretted hydrogen. The affinity of hydrogen in the act of liberation from water is so exalted, that it will combine with and carry over minute traces of carbon, sulphur, phosphorus, selenium, silicon, arsenic, iron, zinc, and other substances, although in the state of free gas it has no tendency whatever to combine with them. The production of silicide of hydrogen, as well as of the tartaric, acetic, oxalic and other ethers, depends on the influence of the nascent state in effecting the combination of bodies.

What is a Chemical Compound?—The answer to this question is involved in the inquiry—How may a chemical compound be distinguished from a mechanical mixture? In gun-cotton (pyroxyline) and gunpowder we have illustrations of the two states. Gun-cotton is a chemical compound of the organic substance (cotton) as a base with the elements of nitrous or hyponitric acid (NO_4). The constituents cannot be separated without an entire destruction of the substance. Gunpowder is a mechanical mixture of charcoal, sulphur, and nitre, in certain proportions, the two last being easily separable from each other and from the charcoal, by appropriate solvents. The chemical force is only brought into operation among these ingredients by heat; while in gun-cotton this force already binds together the nitrous acid and the cotton, and heat merely produces a new series of combinations.

In spite of these broad distinctions, there are some cases of the union of substances, of so doubtful a character, that chemists are not agreed upon the nature of the force which binds them together. Gelatinous alumina, shaken with solution of cochineal, removes the color and is precipitated with it. Charcoal in the same way removes the color of indigo, litmus, cochineal, and of other vegetable and animal substances. It will also remove the blue color of iodide of starch, and the red color of permanganate of potash, which are chemical compounds. This is commonly described as a surface action or an attraction between surfaces, as the properties of the bodies undergo no change.

When caoutchouc is combined with sulphur at a temperature of about 300°, a compound known as vulcanized rubber is produced. The properties of this substance are different from those of its constituents. Thus after vulcanization the rubber is altered in color; its elasticity is remarkably increased; it does not melt even at the boiling point of mercury, and it does not become stiff in the cold. It is also quite insoluble in all the liquids which dissolve rubber. Here then is a change of properties sufficient to justify a chemist in regarding this as a chemical compound of its two constituents. On the other hand, the two substances do not combine in definite proportions: the sulphur may be in the proportion of from 10 to 16 per cent., and it may be removed from the rubber, after incorporation, by the usual solvents, without materially affecting its properties. These conditions are adverse to the hypothesis of a chemical union, and the result is, that such a compound can be expressed by no chemical formula. Again, in the phenomena of solution or diffusion, as of hydrated sulphuric acid, or of anhydrous alcohol in water, we have evolution of heat and a great alteration of volume. Is this a chemical union of the liquids with the water, or is it not? The phenomena accompanying the mixture point to something more than a mechanical force; but there is no change of properties, and there is no evidence of union in definite proportions. This subject is, however, of sufficient importance in a chemical point of view to receive a separate examination.

SOLUTION.—The solution of solids in liquids, whether the solvent be water, alcohol, ether, benzole, chloroform, or mercury, has been assigned by some chemists to a species of affinity, and by others to a physical effect of adhesion. By solution we are simply to understand a combination of a solid with a liquid, in which the solid itself assumes a liquid form. There is no change of properties, and here the great feature of chemical affinity is wanting:—thus common salt dissolved in water possesses all its usual characters. This observation applies equally to the solutions of other salts, as well as to solutions of acids and alkalies. The best solvents are generally those liquids which are similar in properties to the solid. Benzole and oil of turpentine readily dissolve caoutchouc and other solid hydrocarbons; oils dissolve fats; mercury dissolves metals; alcohol dissolves resins; and water, itself a neutral oxide, dissolves neutral salts and neutral compounds, such as gum, sugar, &c. Water is the great solvent for chemical purposes, and it is by the use of this liquid that most chemical changes are produced among solids; it breaks up the cohesion of solids more effectually than pulverization, and thus brings their particles within the sphere of each other's attraction.

Solution is only influenced by gravitation, when the solid salt is allowed to remain at the bottom of the water. The lower stratum of liquid then contains a much larger quantity of the salt than the upper portion; but after a time it will spread by diffusion, varying in degree with the nature of the salt. For this reason, solution is always best effected by suspending the solid substance in the upper stratum of liquid. When the salt is once dissolved and equally diffused throughout the liquid by agitation, gravitation is not found to affect it. Thus, although corrosive sublimate has a specific gravity six times greater than water, yet a solution of it, preserved for many years in a long tube, was not found to contain any more of this salt in the lower than in the upper stratum.

Each substance has its own specific solubility which varies with temperature. As a general rule heat increases the solubility of solids in water, but there are some exceptions. Thus lime, citrate of lime, sulphate of lime, and sulphate of soda, are less soluble at the point than at lower temperatures; while chloride of sodium is equally soluble at a high and low temperature. Solution is sometimes attended with great loss of heat by reason of the salt rapidly passing from the solid to the liquid state. Some of the cheapest freezing mixtures, in the absence of ice, are based upon this property. Thus one part of crystallized nitrate of ammonia, dissolved in one part of water causes the thermometer to fall from 50° to 4°; and five parts of sal ammoniac with five parts of nitre, dissolved in sixteen parts of water, are nearly equally effective. These are anhydrous salts, so that the result is the direct effect of solution, and it appears to point rather to chemical combination than mechanical adhesion. Another fact observed by Playfair and Joule is, that salts containing water of crystallization, when dissolved in water, add no more bulk to the water than is equivalent to the water of crystallization (calculated as ice) with which their atoms are chemically combined. Thus, when alum is dissolved in water, the increase of volume in the solution is not in proportion to the bulk of alum used, but to the bulk of combined water as ice (24 equivalents), contained in it. The atoms of alum have therefore disappeared, or been received within the interstices of the atoms of water; at any rate they occupy no appreciable space. If these results are confirmed, it will show that the hypothesis of mechanical adhesion of a liquefied solid to a liquid is not in all cases sufficient to explain the phenomena of solution. The effect of heat in increasing or diminishing solubility, the fixed limit of solubility for different salts, and the decrease or increase occasionally observed in the volume of the solvent, as well as the singular fact observed by Dr. Gladstone (*Proc. R. S.*, vol. 9, p. 69), namely, the absorptive power on light exhibited by strong solutions of salts, are adverse to the hypothesis of a mere adhesion of atoms.

When a liquid will dissolve no more of a solid, it is said to be *saturated;* in other words, its adhesion or affinity for the solid is exhausted. It is a curious fact, however, that water which is saturated with one salt has still the property of dissolving a second and a third salt. Crystals of nitre may be thus freed from impurities, such as chloride of sodium, by washing them with a saturated solution of nitre. A saturated solution of a salt exerts a powerful attraction on water. If a saturated solution of sulphate of copper is inclosed in a funnel tube, secured at the larger end by bladder, and the tube is plunged in a vessel containing water, so that the liquids inside and outside are on a level, in the course of some hours it will be found that although some of the copper-salt has passed out through the pores of the bladder, a much larger proportion of water has passed in. Solutions of common salt, sugar, and other substances, present this phenomenon, to which the term *endosmosis* (ἔνδον within and ὠθέω to push) has been applied. The diffusion of liquids or their relative tendency to mix on contact has been fully examined by Mr. Graham (*Quart. Jour. Chem. Soc.*, vol. 3, p. 60); and the effect of porous membranes in allowing liquids or dissolved solids to traverse them, has also been made the subject of experiment by the same chemist. Mineral substances, such as arsenic, may thus be separated from organic matter. He has called this process *dialysis.* (*Proc. R. S.*, 1861, vol. 11, p. 243.)

The dissolved solid may be separated from the solvent by the addition of another liquid. Camphor is separated from its solution in alcohol by adding water—gum from its solution in water by the addition of alcohol—soap from water by chloride of sodium, and corrosive sublimate and chloride of gold from water by ether. In the latter case, the metallic salt changes its solvent, and the compound of mercury or gold is found dissolved in the ether as chloride.

When liquids mix together, they are said to combine by *diffusion*, according to various circumstances. Alcohol and water readily combine with evolution of heat and contraction of volume. If 54 parts, by measure, of alcohol, are mixed with 50 of water, the reduction in volume on cooling, is equal to four per cent. (*Mitscherlich.*) This cannot be regarded as the mere result of adhesion or any mechanical force, but rather of chemical union, although the properties of the mixture have undergone no change. If the alcohol be poured carefully on the water in a long tube, and a piece of white wax dropped through the spirit, to indicate, by floating, the exact level of the water, many months may elapse without the position of the wax undergoing a change, and therefore without combination of the two liquids. This depends on the smallness of the area of contact, and the great difference in the specific gravity of the two liquids. Water will dissolve or combine with alcohol in all proportions, but with ether there is a fixed limit: of this liquid it cannot hold dissolved more than ten per cent. by volume. When water is added to a mixture of ether and alcohol, the alcohol is entirely dissolved, but the surplus ether is separated, and floats on the top of the liquid. Chloroform is soluble in alcohol, but only to a limited extent in water; hence, for the same reason, water separates it from alcohol.

Some substances appear to be held in water by a kind of suspension resembling solution. Thus starch forms an opaque liquid; gelatin, gelose, and certain silicates as well as silicic acid itself, are similarly suspended without having formed a perfect combination with the water as a solvent. They appear to constitute hydrates of the respective substances with a large surplus of water. For all practical purposes in chemistry they are regarded and treated as solutions, although the substances may be ultimately deposited in an insoluble form. When a chemical change takes place on the mixture of a liquid and solid, as on the addition of nitric acid to copper or silver, the term solution is no longer appropriate; the liquid is decomposed, and a new compound results.

Solutions of metals in mercury are called *Amalgams*. Some metals are more soluble in this liquid than others; thus gold, silver, tin, and bismuth are rapidly dissolved, while iron, and copper (in its ordinary state), are not affected. Although treated as solution, or the simple adhesion of metal to mercury, as of salt to water, there is every reason to believe that there is a chemical union of the mercury with the metal in definite proportions, and that this compound is dissolved in the large proportion of mercury which forms a liquid amalgam. Tin and silver combine with small proportions of mercury to form crystalline compounds. If a large quantity of mercury is employed, both tin and silver disappear as by solution; but when a smaller proportion is used a soft amalgam is formed, which gradually becomes hard by crystallization. The force which holds the tin to the mercury cannot be considered the same as that which holds the amalgam of tin and mercury to a surface of glass. The solution of metals in mercury is sometimes attended with the production of heat and cold, as well as with a change of state. If equal parts of sodium and potassium are well mixed by pressure under naphtha, and a globule of mercury is poured on the soft alloy, there is instant chemical union with an evolution of heat and flame, and the production of a solid amalgam. Melt together 207 parts of lead, 118 of tin, and 284 of bismuth. These form, when cold, a brittle alloy. When this is reduced to a fine powder, and mixed with 1617 parts of mercury, at a temperature of 60°, the thermometer falls to 14°. This is owing to the rapid conversion of the solid metals to the liquid state, and the absorption of heat from surrounding bodies. It resembles, in effect, the solution of crystallized nitrate of ammonia in water. Mercury, under certain conditions, dissolves the gases hydrogen and nitrogen in the proportions of one equivalent of nitrogen to four of hydrogen. It then becomes semi-solid, and assumes a crystalline condition, like that which it acquires in combining with a large quantity of tin or silver. The union is only of a temporary nature.

Most solids and liquids manifest a tendency to enter into union or combination. There is, however, one substance which shows a remarkable indifference to combination of any kind, and from this indifference it has received the name of paraffine (*parum affinis*).

Proofs of Chemical Change.—We generally look for certain *visible* results as evidence of the chemical union or separation of substances; but the chemical force may have acted without causing visible changes; and on the other hand the condition of allotropy (see page 30) in elements and compounds, shows us that such changes may take place without reference to the chemical force. Photographic chemistry furnishes a remarkable instance of the operation of chemical affinity, without any apparent physical alteration in the condition of the compound. A dried film of pure iodide of silver on glass, after it has received an impression from light, will retain its surface unaltered for many hours, or even days; we should not be able to distinguish the exposed from the unexposed film; but if the exposed surface is washed with a weak solution of pyrogallic acid or sulphate of iron, the silver is reduced and blackened only in the parts which have received the luminous impression, and in a degree precisely proportioned to the intensity with which the impression has been made. There is perhaps nothing so wonderful in the whole range of chemistry as the fact of thus revealing a dormant image which has been produced without any apparent physical change in the iodide of silver by the chemical rays of the spectrum. As a general rule, we cannot trust to our senses as furnishing evidence of the chemical force being brought into operation. We can only arrive at a knowledge of this fact by a process well-known under the name of *analysis* (ἀνὰ λύω to separate), by which we separate the component parts of a body. This may be either *qualitative*, to determine the nature, or *quantitative*, to determine the proportions, of the ingredients. Our analytical results may be confirmed by *synthesis* (σὺν τίθημι to put together), *i. e.*, by reconstructing the substance from its constituent parts. The latter process is not always available, and it is not indispensable to a correct view of the constitution of a body. It is sufficient if we examine the products of chemical combination, and compare their weights and chemical properties with those of their constituents. The following experiment will serve as an illustration of the processes of analysis and synthesis. Place in two Florence flasks some powdered chloride of ammonium. Mix the chloride of one flask with its bulk of dry lime, and apply a spirit-lamp to the mixture. Ammonia, as a gas, will escape. Now add to the chloride in the other flask sufficient sulphuric acid to moisten the powder. Fumes of hydrochloric acid immediately escape. On bringing near to each other the mouths of the flasks, the gases immediately combine to reproduce, by *synthesis* in the air the chloride of ammonium which had undergone *analysis*, or been resolved into its constituents in the two flasks.

Single Affinity.—The chemical force is usually studied under the heads of single and double affinity; and all analytical processes are dependent upon a knowledge of the laws which govern these operations. In single affinity—of three substances present, one is found to combine with another in preference to a third. Let us assume that the three substances are the base baryta in solution and two acids—*i. e.*, the sulphuric and nitric acids diluted with water. On adding the solution of baryta to diluted nitric acid, there is no visible change; the base enters into a soluble combination with the acid, forming nitrate of baryta. When the baryta is added to sulphuric acid, a white insoluble precipitate appears (sulphate of baryta). Both the acids therefore combine with the base, the one to form a soluble, and the other an insoluble salt. If we now wish to discover which of the acids has the stronger affinity for the base, we add sulphuric acid to the solution of nitrate of baryta, and an insoluble sulphate of baryta immediately appears—the nitric acid being set free. If we treat the precipitated sulphate of baryta with nitric acid, it will undergo no change. A minute quantity of the precipitate may be dissolved, but the sulphuric acid still remains, combined with the baryta. The only conclusion to be drawn from these facts, is, that sulphuric acid has a stronger affinity for baryta than nitric acid, and that it will take that base to the entire exclusion and separation of the nitric acid. As a kind of choice is thus manifested, this has also received the name of elective affinity. The change is represented by the following equation, $BaO,NO_5+SO_3=BaO,SO_3+NO_5$.

The term *precipitate* has here been employed to indicate chemical change, and it is desirable to define the proper meaning of a term which so frequently occurs in chemical language. It is applied by chemists to signify that condition in which a substance dissolved in a liquid, is thrown down in a solid form as the result of chemical change or decomposition. If the substance is not dissolved, but diffused mechanically through the water, its falling to the bottom is not true precipitation but subsidence, or the mere effect of its greater specific gravity.

Precipitation always implies that the compound formed is less soluble in the liquid than the substance which produces it. Sulphuric acid added to lime-water produces no precipitate, because sulphate of lime is more soluble than lime. If carbonic acid is employed, there is an immediate precipitate, the carbonate of lime being much less soluble than lime. Precipitation may occur rapidly or slowly, according to the solubility of the precipitate. It may take place as the result of natural causes: thus in petrifying springs, which owe their properties to carbonate of lime, dissolved by carbonic acid in the water, a precipitate of carbonate of lime takes place in the form of stalactite, owing to the escape of carbonic acid. The Geyser water in Iceland deposits silicic acid, and all chalybeate waters produce, on exposure to air, ochreous deposits of hydrated peroxide of iron, under similar circumstances. The quantity of water present, influences the production of a precipitate. A diluted solution of a salt of lime is not precipitated by sulphuric acid, while an equally diluted solution of a salt of baryta is precipitated, the difference depending on the relative insolubility of the sulphates. The great insolubility of chloride of silver, renders it easy to detect the minutest traces either of hydrochloric acid or silver. According to Mitscherlich, one part of hydrochloric acid diffused through 113 million parts of water, is rendered visible, as a white cloud, by the addition of a salt of silver.

The order of affinity of *sulphuric acid* for bases, may be thus easily determined by experiment; and upon this principle, tables of affinity have been constructed, in which the substance whose affinities are to be represented is placed at the head of a column, and the bodies with which it combines beneath it, in the order of their respective attractions; thus the affinity of *sulphuric acid* for several bases is shown in the table. From this it would appear that *baryta* separates sulphuric acid from its compounds with all the substances below it, and that *ammonia* is separated by all those which are above it. It will be found, however, by experiment, that if a solution of ammonia is added to a solution of sulphate of magnesia, there is a precipitate of magnesia. If, on the other hand, magnesia is boiled in a solution of sulphate of ammonia, the magnesia combines with the sulphuric acid, and ammonia is evolved as a gas. Hence the table rather shows the order of decomposition under one set of circumstances. The relative affinity of the acid for magnesia or ammonia will depend on the temperature of the mixture. If we take the base soda, and examine the affinity manifested by it to the three acids—namely, the boracic, sulphuric, and hydrochloric—we find that this becomes also a question of temperature.

SULPHURIC ACID.
Baryta.
Strontia.
Potassa.
Soda.
Lime.
Magnesia.
Ammonia.

SODA AT 60°.	SODA AT A RED HEAT.
Sulphuric.	Boracic.
Hydrochloric.	Sulphuric.
Boracic.	Hydrochloric.

The result depends on the relative fixedness and solubility of the acid at the temperature to which the mixture is exposed. If sulphuric or hydrochloric acid is boiled with borate of soda—on cooling the liquid, the boracic acid is precipitated by reason of its insolubility in water at a low temperature; and sulphate of soda or chloride of sodium remains dissolved. If, however, the precipitated acid be mixed with the solid sulphate, or chloride obtained by evaporation, and the mixture is submitted to a full red heat, borate of soda is reformed, and the more volatile sulphuric and hydrochloric acids are entirely expelled. The fixedness of boracic acid at a high temperature here causes a reversal of the order of combination.

These tables are of great use in analysis, inasmuch as the exceptional cases are not numerous, and are easily remembered. They may be made applicable to elements as well as compounds. We here give a table representing the order of affinity of lime for four common acids; also for some of the combinations of hydrogen with non-metallic bodies, and of nitric acid and oxygen (NO_6) for various metals:—

LIME IN SOLUTION AT 60°.	HYDROGEN.	NITRIC ACID AND OXYGEN.
Oxalic.	Chlorine.	Zinc.
Sulphuric.	Bromine.	Copper.
Acetic.	Iodine.	Mercury.
Carbonic.	Sulphur.	Silver.

The results thus arrived at are often susceptible of important practical applications. The liquid in which a salt is dissolved may cause a reversal of the order of affinity. Thus, if to a strong solution of carbonate of potassa in *water*, we add acetic acid, carbonic acid is expelled, and acetate of potassa is formed and dissolved ($KO,CO_2+\overline{Ac}=KO,\overline{Ac}+CO_2$ in water). If, however, we pass a current of carbonic acid gas for some time into a saturated solution of acetate of potassa in *alcohol*, the gaseous displaces the liquid acid, and carbonate of potassa is reproduced ($KO,\overline{Ac}+CO_2=KO,CO_2+\overline{Ac}$ in alcohol). The insolubility of the alkaline carbonate in alcohol, and its immediate removal by precipitation, appear to explain this change in the order of affinity. If water is added to the alcoholic liquid, the precipitated carbonate is redissolved.

Oxide of lead combines readily with carbonic and acetic acids, forming a carbonate and an acetate of lead. If acetic acid is added to carbonate of lead, the carbonic acid is displaced, and acetate of lead is formed; but if a solution of acetate of lead is exposed to an atmosphere containing carbonic acid, carbonate of lead is formed and the acetic acid is expelled. The manufacture of white lead (carbonate of lead) depends upon this reversal of affinity. The metal is exposed to the fumes of acetic acid, and the formation of an acetate is the first step in the production of a carbonate.

This fact appears to support the view of those who believe that chemical affinity between substances is to some extent governed by the relative proportion or mass of the displacing agent. The changes which chloride of silver undergoes by exposure to light, also tend to corroborate this opinion. When not absolutely dry, chloride of silver, which is of snow-white appearance, is darkened by exposure to light. In fact it is superficially converted to subchloride ($2AgCl=Ag_2Cl+Cl$). The quantity of chlorine thus set free is small. Rose found, by using a delicate balance, that there was no difference in weight between the white and dark chloride. Chlorine water added to the dark chloride renders it again white.

Decomposition by single affinity may take place, although it is not manifested by the precipitation of a solid or the visible escape of gaseous matter. If we boil gold-leaf with some crystals of nitre dissolved in water, there is no change; if we boil the gold in pure hydrochloric acid, there is no change; but if the two are mixed the gold is immediately dissolved. The solution of the gold proves that chlorine has been evolved. This could only proceed from the decomposition of a part of the hydrochloric acid by the nitrate of potash. Under ordinary circumstances a watery solution of nitre may be mixed with hydrochloric acid without any perceptible decomposition of either body.

An interposed animal membrane does not prevent the manifestation of this force. If a tube containing a weak acid solution of acetate of lead is well secured at the mouth with a piece of bladder, and the outer surface of the bladder is then placed downwards on a clean surface of metallic zinc,—in the course of a short time crystals of lead will be deposited on the bladder inside the tube; and the solution will contain acetate of zinc, a fact which proves that the zinc has traversed the bladder either as oxide or metal, and has displaced an equivalent proportion of lead in the solution. This is effected by a capillary *exosmosis* of a part of the solution of acetate of lead, and its simultaneous conversion into acetate of zinc.

Predisposing Affinity.—If zinc is covered with hydrochloric acid it displaces the hydrogen, which escapes, and chloride of zinc is formed; if covered with water, this liquid is not decomposed until an acid is added, when hydrogen immediately escapes, and an oxysalt of zinc is produced and dissolved. This has been called *predisposing affinity*, but it should rather be regarded as concurrent affinity. Two affinities are here brought into play: there is the affinity of zinc for oxygen, and of the acid for oxide of zinc, and these are sufficient to decompose the water. This principle is the basis of many chemical operations. In the manufacture of aluminum, carbon as charcoal cannot alone remove the oxygen from alumina (the oxide of aluminum); but if chlorine is passed over a mixture of alumina and charcoal heated to a high temperature, the carbon readily takes the oxygen, and the chlorine now combines with the aluminum. Platinum cannot be made to unite to oxygen directly; but, if caustic potash is fused on the metal, this is oxidized and destroyed by reason of the tendency of the alkali to combine with oxide of platinum.

Double Affinity.—In double affinity there is a reciprocal interchange of elements, or, in reference to salts, of acids and bases, so that two new compounds are produced. One of the simplest cases is seen on the admixture of hydrochloric acid and a solution of soda. Chloride of sodium and water result ($NaO+HCl=NaCl+HO$). Among numerous instances which may be taken from the class of salts, there is the reaction of sulphate of potash on nitrate of baryta, by which sulphate of baryta and nitrate of potash are produced ($KO,SO_3+BaO,NO_5=BaO,SO_3+KO,NO_5$). In this case *one* insoluble salt only is formed and precipitated; but two soluble salts may be changed into two perfectly insoluble compounds, as in adding a solution of sulphate of silver to chloride of barium (both soluble) when sulphate of baryta and chloride of silver (both insoluble) result. Thus $AgO,SO_3+BaCl=BaO,SO_3+AgCl$. This decomposition forms one of the steps in the production of pure peroxide of hydrogen. Double affinity generally furnishes to the chemist a more perfect method of decomposition than single affinity. Thus oxalate of ammonia more effectually precipitates lime than oxalic acid. A solution of arsenious acid does not readily decompose solutions of sulphate of copper or nitrate of silver; but if the acid is combined with a small quantity of alkali (ammonia), the precipitation of insoluble arsenites of the metals by double affinity is immediate and complete.

In general it may be inferred that two salts will decompose each other, when, by interchange, an insoluble compound or precipitate can result. Solubility, however, is a purely relative term, and precipitation must therefore often depend on the quantity of water present in the saline solutions. Nitrate of baryta gives a dense white precipitate with a solution of borate of soda, provided the two solutions are concentrated. If much water is present, there will be no precipitation on mixture; a fact also proved by the re-dissolution of the precipitate on adding a quantity of water. Sulphate of soda will precipitate a salt of lime, and chloride of platinum a salt of potassa, provided the respective solutions are concentrated; but if much diluted, there will be no precipitate. The platino-chloride of potassium, although precipitated from potassa or its salts, by a solution of chloride of platinum, is sufficiently soluble in boiling water to precipitate from their solutions the salts of rubidium and cæsium, the platino-chlorides of which metals are far less soluble than the corresponding salt of potassium. This, in fact, is the only available method of separating the salts of the two new metals from the salts of potassium. While the degree of dilution always affects the production of a precipitate, it sometimes so completely changes its character that it might be fairly inferred that two different compounds were under examination. Thus if nitrate of silver is added to a concentrated solution of borate of soda, a white borate of silver is precipitated: if the solution of borate is much diluted, nitrate of silver gives a brown precipitate resembling oxide of silver. Sulphocyanide of potassium produces, in a concentrated solution of a salt of copper, a black precipitate of sulphocyanide, which slowly becomes gray and white; in a moderately diluted solution a gray precipitate is thrown down, and in a very diluted solution a white precipitate of sub-sulphocyanide is slowly formed.

Precipitates are sometimes readily dissolved by the precipitant: thus the scarlet iodide of mercury is easily dissolved by a solution of iodide of potassium. This renders it necessary to employ tests with caution, or the presence of a substance may be overlooked. When the double decomposition of two salts does not take place in the cold, it may be brought about by heating the mixture.

Double affinity is liable to be modified by all the causes which affect single affinity. If a mixture of dry chloride of sodium and sulphate of ammonia is heated, chloride of ammonium is sublimed, and sulphate of soda remains. This is one method of manufacturing sal ammoniac from the ammoniacal liquor of gasworks. When the two salts are intimately mixed with a small quantity of water the temperature rises, and the mass rapidly dries. There is a double decomposition, and the sulphate of soda produced absorbs water of crystallization. Each of the salts alone lowers the temperature during the act of solution (*Chem. News*, Sept. 15, 1860.) But when powdered sulphate of soda is well mixed with chloride of ammonium at 60°, there is a reversal of the affinities,—anhydrous sulphate of ammonia and common salt are produced, while the water of crystallization of the soda-sulphate is set free, the mass acquiring a liquid consistency. (See page 33.) When solutions of these two salts are mixed, there is, according to Schiff, an increase of volume owing to the setting free of water of crystallization.

Salts having the same acid or base do not precipitate each other. Thus a solution of sulphate of lime does not decompose sulphate of soda or chloride of calcium. On this principle, the last mentioned salt is employed to determine whether the alkalinity of river-water depends on the presence of the carbonate of potassa or soda, or of the bicarbonate of lime. In the former case, it gives a precipitate; in the latter none.

But double affinity may be exerted between two salts in cases in which there is no visible change or decomposition. When a solution of nitrate of soda is mixed with chloride of potassium, and this mixture is boiled, chloride of sodium, or common salt, is separated, because it is the least soluble of the salts at a boiling temperature, and therefore requires the largest amount of water to hold it in solution. (See page 29.) If the saturated solutions of the two salts are kept at a low temperature, nitrate of potassa crystallizes out of the liquid. In either case there is an interchange of acid and base dependent on the relative solubility of the salts at a given temperature ($NaO,NO_5+KCl=NaCl+KO,NO_5$). The process above mentioned, has been employed in Prussia for the manufacture of nitre. The manufacture of sulphate of magnesia from sea-water is dependent on a similar decomposition. Sulphate of soda added to a solution of chloride of magnesium or bittern, produces no visible change; but when boiled, the compounds are resolved into chloride of sodium and sulphate of magnesia. The former is separated by evaporation of the liquid at the boiling-point, the latter by allowing the cold saturated solution to deposit crystals ($NaO,SO_3+MgCl=NaCl+MgO,SO_3$).

The production of a color on the admixture of colorless solutions of salts is evidence of at least a partial interchange of acids and bases. A very diluted solution of ferrocyanide of potassium added to extremely diluted solutions of sulphate of copper or persulphate of iron, produces in the one case a red, and in the other a blue color in the liquid. These results furnish chemical proofs that the ferrocyanogen of the potassium-salt has, at least in part, united to the metals of the copper and iron salts. Sulphocyanide of potassium may be substituted for the ferrocyanide in reference to iron; and in this case a blood-red color, but no precipitate, results. Berzelius long since devised an ingenious experiment by which the interchange of acid and base in two salts was clearly proved by the peculiar color acquired on mixture. Of the diluted solutions of the salts of copper, the nitrate and sulphate remain blue when boiled; but the diluted chloride, which is blue at 60°, acquires a bright green color at 212°. This change of color is therefore a distinguishing test among these salts, of the presence of *chloride* of copper in a diluted state. A solution of chloride of sodium is colorless and remains so at all temperatures. When a diluted solution of nitrate of copper is added to a diluted solution of chloride of sodium and the mixture is heated, it acquires a bright green color, thus proving that some portion at least of the nitrate of copper, must have been converted to chloride of copper, and therefore that an interchange of acids and bases must have taken place. If the two solutions are highly concentrated, the interchange takes place at 60°, since the mixture in the cold has a greenish color—the color of the chloride of copper when in a more concentrated form.

We have hitherto treated the saline compounds as if both were soluble in water; but cases of double affinity are witnessed, in which one salt is soluble and the other is insoluble. If insoluble sulphate of baryta or oxalate of lime is boiled in distilled water with soluble carbonate of potassa for a short time, and the respective liquids are filtered—it will be found that a partial interchange of acids and bases has taken place, and while the filtrates (the filtered liquids) will contain two soluble salts (the carbonate of potassa associated either with the sulphate or oxalate of potassa), the white residues on the filters will contain, besides sulphate of baryta and oxalate of lime, the insoluble carbonates of baryta and lime. Four salts are in each case produced, as represented in the following equation, in which the decomposition is given only for the sulphate of baryta, $2BaO,SO_3+2KO,CO_2= \underbrace{KO,SO_3+KO,CO_2}_{\text{Soluble.}}$ and $\underbrace{BaO,SO_3+BaO,CO_2}_{\text{Insoluble.}}$. This mode of decomposition is sometimes resorted to, in order to render an insoluble compound sufficiently soluble for the purpose of testing. The silicification of chalk or soft limestone is based on this principle. The mineral is soaked in water-glass, or a solution of silicate of potash or soda, and it is afterwards exposed to the air; silicate of lime and bicarbonate of potassa result. The surface of the chalk is thus hardened and rendered impermeable to water. It is probable that the presence of Epsom salt, or sulphate of magnesia, in spring waters in certain districts, is dependent on a natural reaction of this kind. Water containing sulphate of lime flowing over a bed of magnesian rock (carbonate of magnesia) becomes impregnated with sulphate of magnesia, a portion of the lime being exchanged for this base. If carbonate of magnesia is agitated with a solution of sulphate of lime, sulphate of magnesia will soon be found in the filtered liquid, by appropriate tests.

Double affinity is not prevented by the interposition of animal membrane. If the mouth of a tube containing sulphate of soda is well secured with bladder, and inverted in a vessel containing a solution of nitrate of baryta—or if the nitrate of baryta be secured in a tube, and the soda-sulphate is placed in an open vessel, double decomposition is observed to take place. In performing this experiment many times, however, we have noticed that the white precipitate of sulphate of baryta has been formed in the tube containing the nitrate, and not in that containing the sulphate of soda.

Catalysis (from κατὰ downwards, and λύω to loosen) is a term which was first employed by Berzelius, to explain those cases in which two or more bodies are combined by the presence of a substance which itself takes no share in the chemical changes. A body is thus supposed to resolve others into new compounds merely by contact, without gaining or losing anything itself. When a mixture of oxygen and hydrogen is exposed to the action of spongy platinum, the gases combine to form water; when alcohol is dropped on platinum-black under exposure to air, the alcohol is oxidized and converted into acetic acid; when a ball of spongy platinum, made red hot, is placed on a mass of camphor, it continues to glow, and causes a slow combustion of the camphor; when a ball of platinum is made white hot and plunged into water, it causes the separation of the constituent gases oxygen and hydrogen; and lastly, when fine platinum wire is heated red hot, and exposed to a mixture of coal-gas and air, it continues to glow, and leads to a slow combustion of the gas. In these cases the platinum has produced combination as well as decomposition, but it has undergone no change. We have witnessed a similar effect with charcoal placed in a mixture of oxygen and sulphuretted hydrogen. The gases were combined with explosion, but the charcoal underwent no change. The power of charcoal to absorb and remove foul effluvia, by leading to their oxidation, may be regarded as a similar phenomenon; but all these are simple cases of the absorption and condensation of gases by the platinum and charcoal, and are not referable to any new force or to any occult effect of contact or presence.

Sulphur, it has been already stated (p. 44), will unite at a high temperature to India-rubber, and will then produce in it the effects indicated by the term vulcanization—*i. e.*, change of color, infusibility, great increase of elasticity, and a resistance to heat and cold. The vulcanized rubber when boiled in a solution of sulphite of potash is desulphured; it reacquires its usual appearance, but it still retains the properties which the sulphur imparted to it. This has been ascribed to a catalytic action, for the sulphur itself has undergone no change.

The production of anhydrous chloride of magnesium, according to Mitscherlich, turns upon a similar state of circumstances. If hydrochloric acid is saturated with hydrate of magnesia, and the liquid is concentrated and cooled, large crystals of chloride of magnesium combined with water are obtained. If these crystals are heated, like those of other chlorides, in order to expel the water, the hydrochloric acid escapes and magnesia remains. If, however, equal weights of hydrochloric acid are saturated with magnesia and ammonia, and the two solutions are mixed and evaporated to dryness, the residue, when heated to fusion in a platinum crucible, consists entirely of anhydrous chloride of magnesium; the whole of the chloride of ammonium having been expelled. Here chloride of ammonium causes a fixed combination of the elements, apparently by a catalytic force.

Catalytic results are obtained with *compounds* as well as with simple substances. The production of oxygen at a low temperature, from a mixture of peroxide of manganese, or of iron with chlorate of potash, has been referred to an action by catalysis or presence. The facts, however, admit of another explanation.—(*See* OZONE.) The decomposition of peroxide of hydrogen by contact with a variety of metals and oxides, was generally explained by reference to catalysis, until the recent views of Schönbein had been made public.

The term catalysis has been applied by some chemists to changes wrought by a substance which itself undergoes a change during the process, although it ultimately passes to its original condition. Finely powdered hydrated peroxide of iron, when heated on metallic-gauze, and placed over a capsule containing ether, alcohol, or pyroxylic spirit, was found by Mr. Ashby to cause the oxidation of these liquids, and to maintain slow combustion for several hours, over a surface of 120 square inches. (*Proc. R. S.*, vol. 7, p. 324.) The compound was as effectual in this respect as platinum itself. The cause of the phenomenon, however, was found by him to depend on the conversion of the peroxide into the magnetic oxide of iron, and the reconversion of this into peroxide by absorbing oxygen from the air. He found that an old nail entirely transmuted to rust, would produce the same effect; and he has suggested that from this cause, cases of spontaneous combustion may arise as a result of the escape of inflammable vapors in the vicinity of masses of rusty iron.

The hydrated peroxide of iron is extensively used for the purification of coal-gas from sulphide of hydrogen. The iron is converted into sulphide by the absorption of this gas, and water is produced. On exposure to air the sulphide of iron is reconverted into oxide, and may be used for many months for the purpose of purification. These effects produced by the oxide of iron are, however, intelligible on common chemical principles.

There are many changes in *organic* compounds which have been referred to catalysis—*e. g.*, the conversion of gum and starch to sugar, of alcohol to ether by sulphuric acid, and of sugar to alcohol by a ferment; but there are here numerous reactions depending on a variety of causes; and as science progresses, and these reactions become better understood, the use of this term may be rendered unnecessary.

Electrolysis.—(ἤλεκτρον, λύω, to loosen by electricity.)—This term is applied to the electro-chemical decomposition of substances as a result of the electric current. The electric fluid serves to unite as well as to disunite bodies; and in producing their disunion or separation there is this remarkable difference from the chemical force—namely, that it transports and collects at particular points, called *poles*, the elements or compounds which are separated.

When the electrodes or poles of a voltaic battery are brought near to each other in certain liquids, such, for instance, as accidulated water and saline solutions; or, in other words, when these liquids are made part of the electric circuit, so that the current of electricity passes through them, decomposition ensues; that is, certain elements are evolved in obedience to certain laws. Thus water, under these circumstances, yields oxygen and hydrogen; and the neutral salts yield acids and alkalies. In these cases, the ultimate and proximate elements appear at the electrodes or poles—not indiscriminately, or indifferently; but *oxygen* and acids are evolved at the *anode*, or surface at which the electricity enters the electrolyte; and *hydrogen*, and alkaline bases, at the *cathode*, or surface at which the electric current leaves the body under decomposition.

All compounds susceptible of direct decomposition by the electric current are called *electrolytes;* and when electro-chemically decomposed, they are said to be *electrolyzed.* Those elements of the electrolyte which are evolved at the *anode* are termed *anïons*, and those which are evolved at the *cathode*, *catïons* (ανίον, that which goes upwards; χατίον, that which goes downwards), and when these are spoken of together, they are called *ïons:* thus when acidulated water is *electrolyzed*, two *ïons* are evolved, oxygen and hydrogen, the former being an *anïon*, the latter a *catïon.*

In all *primary* electro-chemical decompositions, the elements of compounds are evolved with uniform phenomena either at the anode or cathode of the electrolyte; hence their division into *electro-negative* and *electro-positive* bodies, or, into *anīons* and *catīons.* The latter have more recently received the name of *basylous* bodies, as by combining with oxygen they form a large class of bases. But it frequently happens that the evolution of a substance at the electrode is a secondary effect; *sulphur*, for instance, in the decomposition of sulphuric acid, is evolved at the cathode or negative pole, not by *direct* electrolysis, but in consequence of the action of the nascent hydrogen; and whenever sulphur is obtained by primary electrolytic action from a compound containing it, it is evolved at the anode, or positive pole; hence, in classifying the elements according to their electrical relations, this distinction must be observed. It is also necessary to guard against the combination of the substance (or *īon*), with the electrode; hence the advantage of platinum electrodes, that metal being acted upon by very few of them.

The following table of *simple and compound īons* has been drawn up by Faraday:—

ELECTRO-NEGATIVE BODIES OR ANÏONS.

Oxygen
Chlorine
Iodine
Bromine
Fluorine

Cyanogen
Sulphuric acid
Selenic acid
Nitric acid
Chloric acid

Phosphoric acid
Carbonic acid
Boracic acid
Acetic acid
Tartaric acid

Citric acid
Oxalic acid
Sulphur
Selenium
Sulphocyanogen.

ELECTRO-POSITIVE BODIES OR CATÏONS.

Hydrogen
Potassium
Sodium
Lithium
Barium
Strontium
Calcium
Magnesium
Manganese
Zinc

Tin
Lead
Iron
Copper
Cadmium
Cerium
Cobalt
Nickel
Antimony
Bismuth

Mercury
Silver
Platinum
Gold
—
Ammonia
Potassa
Soda
Lithia
Baryta

Strontia
Lime
Magnesia
Alumina
Protoxides generally
Quinia
Cinchonia
Morphia
Vegeto-alkalies generally.

Compounds only undergo electrolysis: and, to act as electrolytes, they must be in a state of solution or fusion. Electrolysis is definite in amount. Thus the quantity of electricity produced during the solution of 32 grains of zinc, is equivalent to the decomposition of 9 grains of water. Electrolytes differ in the facility with which they yield up their elements to the influence of the electric current, or in the resistance which they offer to electro-chemical decomposition. The following bodies are electrolytic in the order in which they are placed, those which are first, being decomposed by the current of lowest intensity:—

Iodide of potassium (solution)
Chloride of silver (fused)
Chloride of zinc (fused)
Chloride of lead (fused)
Iodide of lead (fused)
Hydrochloric acid (solution)
Water acidulated by sulphuric acid.

For an account of the electrolysis and electrosynthesis of water, see Water.

Prismatic or Spectrum Analysis.—Chemists have for many years relied upon the colors given by the salts of various metals, to the colorless flames of alcohol, or coal-gas, as a useful aid to qualitative analysis. MM. Kirchoff and Bunsen, by their recent researches on the colored flames of metals, have arrived at an entirely new method, which, they assert, not only enlarges the scope of chemical reactions, but points to the solution of problems hitherto considered unapproachable by science. This method consists in not merely relying upon the color imparted to the flame, but in decomposing the colored light by a prism; in other words, in submitting the colored flame to a minute prismatic analysis. Their observations have been hitherto chiefly directed to the detection of the metals of the alkalies and alkaline earths. They have employed pure salts of these metals, as well as various mixtures of them, and they have found that the more volatile the metallic compound on which they operated, the brighter was the spectrum which they obtained. A high temperature was generally required: a coal-gas flame of a Bunsen's burner, of which the heat was estimated at 2350° C, was found to be sufficient for the alkaline metals, and the colorless nature of this flame rendered it otherwise well adapted for the spectralytic observations. The alkaline salt in minute quantity was placed on the end of a fine platinum wire (bent into a hook and flattened, if for a solution), and this was introduced into the lower part of the colorless coal-gas flame. The light of the colored flame was then made to traverse a prism of sulphide of carbon, having a refracting angle of 60°; and as it issued from the prism it was examined by a small telescope.

The reader will find a description of this apparatus, and of the method of employing it, in the *Philosophical Magazine* for August, 1860, page 91, and the *Pharmaceutical Journal*, February, 1862; but it has since been superseded by more convenient instruments. The colored flame of each metal, even in the minutest quantities, was found to give a well marked and characteristic spectrum. Compared with the spectrum of solar light, the actual amount of colored light was very small, and this was distributed without any kind of order, in a series of bands or stripes of different widths and intensities, the bands of color taking up the situation of the corresponding spectral colors. Sodium was observed to give a single or a double line of yellow light, only in a position corresponding to the orange rays of the solar spectrum. Potassium, besides a more diffused spectrum, gave a red line in the extreme red rays, and a violet line in the extreme violet rays. Lithium gave a dark spectrum, with only two bright lines, one a pale yellow corresponding to the yellow rays, and the other a bright red corresponding to the red rays. Strontium, barium, and calcium, the only three alkaline earthy metals which give spectra (magnesium not being volatile in this flame), are remarkable for the number and variety of the colored bands which they present. Strontium presents eight characteristic lines—six red in the part corresponding to the red rays, one broad orange band parallel to the orange rays, and at some distance from these a blue line, in the situation of the blue rays. The spectra of barium and calcium are distinguished from the others by the number of green bands which they present. Two of these in the situation of the green rays characterize barium. There are, besides these, three other green bands, and several yellow, orange, and red lines. Calcium presents one broad green band in the situation of the yellow-green rays; and a bright orange band near the red rays, besides several smaller orange lines. The new alkaline metal *Cæsium* (*cæsius*, sky-color), discovered by Bunsen in the waters of Durckheim and Baden, as well as in most spring-waters containing chloride of sodium, presents two distinct grayish-blue lines in the parallel of the blue rays, and no other colored bands or lines. The other new metal, *Rubidium*, found by Bunsen in the waters of Hallein and Gastein, derives its name from the two splendid red lines in its spectrum; these are of a low degree of refrangibility. The optical characters of the spectra are constant for each metal, and are equally well marked in size and position under all varieties of flame, even of that given by the electric discharge.

Bunsen estimated that the amount of sodium which admitted of detection by prismatic analysis was the 1[illegible]5,000,000th part of a grain; of lithium, the 70,000,000th; of potassium the 60,000th; of barium the same; of strontium the 1,000,000th; and of calcium the 100,000,000th of a grain!

The delicacy of the sodium reaction accounts for the fact that all bodies, after a lengthened exposure to atmospheric air, show, when heated, the sodium line. Even ignited air and all kinds of dust show the yellow tinge of sodium. Fine platinum wire or foil, however clean, if exposed to air for a short time, has been observed to give a yellow color to flame, owing, as it is supposed, to the deposit upon its surface of sodium derived from the atmosphere. Three-fourths of the earth's surface are covered with sea-water, and the minutely diffused chloride of sodium may, it is supposed, be thus spread through the whole of the atmosphere. Lithium, which was supposed to be a rare metal, also appears by this mode of analysis to be very widely distributed. Bunsen found it in about an ounce and a-half of the waters of the Atlantic Ocean; in the ashes of kelp from Scotland; the ashes of tobacco, of vine-leaves, and of plants growing on various soils. It was found in the milk of animals fed upon these crops, and it was detected by Dr. Folwarczny in the ash of human blood and muscular tissue. It has also been discovered in the residue of Thames-water, in Stourbridge clay and in meteoric stones. It is a curious fact that the intermixture of these alkaline metallic compounds does not materially interfere with the optical as it does with the common steps of a chemical analysis. Thus a drop of sea-water shows at first a sodium-spectrum; after the volatilization of the chloride of sodium—a calcium-spectrum appears, which is made more distinct by moistening the platinum wire with hydrochloric acid. By treating the evaporated residue of sea-water with sulphuric acid and alcohol, potassium and lithium-spectra are obtained. The strontium reaction is best procured by digesting the boiler-crust of sea-going steamers in hydrochloric acid, and employing alcohol as a solvent. By this process of analysis, most mineral waters are found to contain all the alkalies and alkaline earths excepting the compounds of barium.

The different degrees of volatility in the alkaline metals are favorable to their detection in a state of mixture. Thus a solution containing less than the 600th of a grain of each of the following chlorides—potassium, sodium, lithium, calcium, strontium, and barium—was brought into the flame. At first the bright sodium line appeared, and when this began to fade the bright-red line of lithium was seen, while at some distance from the sodium line the faint red line of potassium came into view, and with this two of the green barium lines; the spectra of the potassium, sodium, lithium, and barium salts gradually faded away, and then the orange and green calcium lines showed themselves in their usual positions.—(*Phil. Mag.*, Aug. 1860, p. 106.)

An improvement has been recently made in the prismatic apparatus by which the spectra of two flames may be examined at once. Thus any doubt respecting the presence of the substance from the colored band in one spectrum, may be removed by introducing a portion of the suspected substance into the second flame, so that the two spectra may be seen side by side, and compared.

It has been also observed that gases ignited by the electric spark from Ruhmkorff's coil give spectra of a remarkable kind. Thus hydrogen through which the electric discharge is passed, gives a spectrum having an intensely red line like lithium, and a bright band of green, which can be split up into a number of thin and beautiful green rays (Roscoe). Spectra of nitrogen, chlorine, and other gases rendered incandescent, have been obtained by various observers, and it is not improbable that gases generally and their complex mixtures may be hereafter qualitatively determined by this method, like the compounds of alkaline metals.

The platinum poles of a battery, simply ignited, give a violet blue platinum spectrum; and if a salt of copper, iron, chromium, nickel, or other metal, be placed upon them, a spectrum peculiar to each metal is brought out, but instead of a few lines of color, as in alkaline metals, they occur in many hundreds. Dr. Roscoe describes seventy brilliant lines in the iron spectrum, of all degrees of intensity and breadth. The most prominent of these lines may, however, be selected for identity. Kirchoff states that he has thus been able to distinguish the compounds of the rare metals—yttrium, erbium, terbium, lanthanum, didymium, and cerium. The spectra obtained from a mixture of the common metals, are not so distinct as those of the alkaline series. Thus in German silver, the spectrum may show only one of the constituents (Roscoe). The spectra of the common metals require a much higher temperature (*i. e.*, the electric spark of Ruhmkorff's apparatus) for their production, and they are then liable to be mixed with the spectra of the platinum poles, as well as those of the metalloids, which constitute the acids or radicals of these salts.

As these discoveries are at present in their infancy, it is difficult to speculate upon the practical results to which they may ultimately lead. In reference to the *qualitative* analysis of the alkaline salts, they will enable a chemist not only to detect the respective metals, with great rapidity, in quantities inconceivably minute; but they may also enable him to detect these quantities in mixtures with each other, with a certainty which no other known analytical process can furnish. On further research they may serve to identify, with nearly equal certainty, the salts of other metals, either alone or in a state of admixture. Quantitative analysis, by the usual processes, must, however, be still resorted to, in order to determine the proportion of ingredients by weight in a compound; and as it is impossible to weigh a smaller quantity than the 1000th part of a grain, chemists may in future be compelled to assign to a compound many substances which do not admit of a determination by weight. The extreme delicacy of this photo-chemical method is likely to create the greatest difficulty in its practical application. When a mineral-water like that of Baden is thereby shown to contain all the metals of the alkalies and alkaline earths, excepting barium, besides two new metals, one of them (the more abundant) existing only in the proportion of one part in a hundred million parts of the water, the question will really be, whether there can be any assigned limits to the number of substances which may be discovered by such a mode of analysis.

CHAPTER IV.

EQUIVALENT WEIGHTS AND VOLUMES—NOMENCLATURE AND NOTATION.

Determination of Equivalent Weights.—It has been already described as a special character of a true chemical compound, that its constituents combine in fixed proportions, which are represented by figures, and are called equivalent or atomic weights. For the determination of these weights, a series of careful analyses of the substance are made. To take *water* as an example, there is no compound in chemistry of which the constitution has been so accurately determined, both analytically and synthetically, as of this. In 100 parts by weight, it is found to contain 11·09 of hydrogen, and 88·91 of oxygen. These proportions reduced to their smallest denomination would be represented by the figures 1 and 8; or if, instead of making hydrogen unity, we assumed that oxygen combined as 1, then hydrogen would be represented by the decimal 0·125. As, however, this last assumption would lead to a very inconvenient use of decimals, the standard of unity is assigned, by most chemists, to *hydrogen:* and the selection of hydrogen has this great advantage, that being the lightest body in nature, and combining relatively in the smallest weight, the figures representing the equivalents of the other bodies are comparatively low and are easily remembered. The numbers 1 and 8 therefore respectively represent the atomic weights of hydrogen and oxygen, on the assumption that one atom of each element is contained in the compound—the weight of the atom of water being therefore 9, the sum of these weights.

All bodies combine either with hydrogen or with oxygen, and the atomic weight of any body may be therefore found by analyzing its compound with either of these elements, and determining by the rule of proportion how much by weight enters into combination with 1 part of hydrogen or with 8 parts of oxygen. The atomic weight of sulphur may be thus determined. 100 parts of its compound with hydrogen (*Sulphide of Hydrogen*) are composed of 94·1 of sulphur and 5·9 of hydrogen: hence 94·1÷5·9=15·9, or, allowing for differences of analysis, 16, the atomic weight of sulphur. Again, hydrochloric acid consists in 100 parts of 97·26 chlorine and 2·74 hydrogen: hence 97·26÷2·74=35·49, or, in round numbers, 36, the atomic weight of chlorine.

It will be understood that these figures do not represent the absolute, but merely the proportional weights in which bodies combine. We have no knowledge of the absolute weight of an atom of any substance, and we are unable to say whether the combining weights thus determined, include one or more atoms of any element; but it is convenient to assume that the figures represent the relative weights of *atoms;* and that however the figures may vary, there is only one atom of each element in the figures which represent its combining weight. We have thus arrived at two of the laws of chemical combination.

1. The equivalent or atomic weight of a body represents the smallest quantity by weight in which it will combine with one part by weight of hydrogen or eight parts by weight of oxygen.

2. The equivalent weight of a compound is the sum of the equivalents of its constituents.

There is a third law which flows from the preceding:—

3. If a simple or compound body combines with more than one proportion of the same substance, the other proportions are multiples, or sub-multiples, of the first.

For an illustration of this law the reader is referred to *Oxides*, under Oxygen.

Guided by these rules, it is possible to determine the atomic weight of a substance (fluorine), which has never yet been isolated. The compound of this body with calcium is a well-known mineral. Assuming that we take a weighed quantity of fluoride of calcium, we convert it into sulphate of lime by heating it with sulphuric acid. The weight of the sulphate of lime being known, the weight of the calcium in the lime is easily determined; and by deducting the weight of calcium from the original weight of fluoride employed in the analysis, the exact amount of combined fluorine is known. The atomic weight of this unknown element is thus found to be 19.

These laws of combination are of great aid to the analyst. If he can determine the weight of one constituent of a compound, the weight of the other may be accurately determined by calculation. If, for instance, in reference to sulphate of lime—should the weight of sulphuric acid be determined, then as 40 parts of sulphuric acid unite to 28 of lime to form this salt; the amount of lime associated with the acid may be readily known by a simple calculation; or, conversely, if the weight of lime is determined, the amount of sulphuric acid which must have been combined with it may be easily calculated.

It was at first supposed that the equivalents of all simple substances would be found to be integers or multiples of hydrogen, taken as unity; but experience, based on accurate analyses made by Dumas, shows that this rule admits of application only to those elements enumerated in the subjoined list, and even the accuracy of the results on which this list is based has been recently called in question:—

Hydrogen. 1.
Oxygen 8. Sulphur 16.
Carbon 6. Phosphorus 32.
Nitrogen 14. Arsenic 75.
Calcium 20.

To this number some chemists have added fifteen other elements. M. Stas, who has recently investigated this subject, denies the existence of any multiples of hydrogen among the equivalent weights. He assigns as the equivalent of nitrogen 14·041, and of sulphur 16·0371. These differences are not, however, such as to affect materially any calculations based on the elements; and with respect to the equivalent weights of other substances, it is the common practice among chemists to represent them by whole numbers. The reason is obvious. No two chemists agree concerning the decimals. The equivalent of chlorine is given at 35·45, 35·47, and 35·50, by equally reliable authorities. It is usually taken at 36. Strontium is given by Stromeyer at 43·67, by Dumas at 43·74, by Rose and de Marignac at 43·77, by Liebig at 43·80, and by Graham and Pelouze at 43·84. It is usually taken at the whole number 44. The whole numbers are easily carried in the memory; and if great accuracy is required in any investigation it is easy to substitute for them, the real figures of any selected authority.

Symbols.—It will have been perceived from frequent examples given in the preceding pages, that a symbolic language has been generally adopted by chemists. Thus the *symbols* H, O, S, Cl, stand respectively as abbreviations for hydrogen, oxygen, sulphur, and chlorine. When the initials of elements are similar, then the first and second, or the first and third letters of the name of the substance are taken: and in reference to the metals the corresponding Latin names are similarly used as distinctive symbols. It is important to bear in mind, however, that these symbols not only represent the element but the relative *weight* of it which enters into combination. Thus the letters HO, not merely represent hydrogen and oxygen, but 1 part of hydrogen and 8 parts of oxygen; and the two associated, 9 parts of water. The number of atoms of each element in a compound is generally indicated by a figure placed on the right-hand corner. Thus the symbol HO_2 indicates 2 atoms of oxygen combined with 1 atom of hydrogen (peroxide of hydrogen), while 2HO represents two atoms of water—the figure thus placed on a line, doubling all that follow it up to the addition sign +, or symbols included in brackets. Thus KO,SO_3, represents sulphate of potassa, but $KO,2SO_3$ represents bisulphate of potassa. Sometimes in order to represent 2 atoms, instead of a figure 2 at the right corner, the symbol is barred, as thus, $\underline{O}.\underline{S}$. These are equivalent to O_2 and S_2. A collection of symbols constitutes a *formula*, as in the formula for alum, $KO,SO_3+Al_2O_3,3SO_3+24HO$. The plus sign is introduced to show that in this compound salt, the elements are arranged as sulphate of potash, sulphate of alumina, and water. It will be perceived from this formula that the *atom* of crystallized alum is compounded of 71 atoms, namely, 40 of oxygen, 24 of hydrogen, 4 of sulphur, 2 of the metal aluminum, and 1 of the metal potassium; and the equivalent weight of the compound calculated from this constitution would be 474·5. Formulæ when so arranged as to represent chemical decompositions, constitute an *equation*, a term borrowed from algebra, to represent that the quantities on the two sides are perfectly equal—*i. e.*, that the formulæ although dissimilar will represent an equal number of atoms, and therefore, equal atomic weights, as in the reaction of common salt on a solution of nitrate of silver, $NaCl+AgO,NO_5=AgCl+NaO,NO_5$. The meaning of the word *equivalent* will be apparent from this equation. It denotes a quantity of one substance which can exactly replace or be substituted for another in chemical combination. Thus silver is substituted for sodium, but in weights which are to each other respectively as 108 to 23, *i. e.*, these weights of the metals are equal to each other in the power of saturating the same quantity of chlorine, *i. e.*, 36: the 8 of oxygen combining with the sodium, and exactly replacing the 36 of chlorine which have been transferred to the silver.

The following Table comprises an alphabetical list of the 65 elements now known to chemists, with their respective symbols, and their atomic or equivalent weights, hydrogen being assumed as unity. In this Table, the non-metallic elements or metalloids are printed in italics to distinguish them from the metals.

Table of Elementary Substances, with their Symbols and Equivalent or Atomic Weights.

ELEMENTS.	Symbols.	Atomic Weights.	ELEMENTS.	Symbols.	Atomic Weights.
Aluminum	Al	14	Molybdenum	Mo	48
Antimony (Stibium)	Sb	129	Nickel	Ni	30
Arsenic	As	75	Niobium	Nb	
Barium	Ba	69	*Nitrogen*	N	14
Bismuth	Bi	213	Norium	No	
Boron	B	11	Osmium	Os	100
Bromine	Br	78	*Oxygen*	O	8
Cadmium	Cd	56	Palladium	Pd	54
Cæsium	Cæ	123	Pelopium	Pe	
Calcium	Ca	20	*Phosphorus*	P	32
Carbon	C	6	Platinum	Pt	99
Cerium	Ce	46	Potassium (Kalium)	K	39
Chlorine	Cl	36	Rhodium	Ro	52
Chromium	Cr	26	Rubidium	Rb	85
Cobalt	Co	30	Ruthenium	Ru	52
Columbium (Tantalum)	Ta	184	*Selenium*	Se	40
Copper (Cuprum)	Cu	32	*Silicon*	Si	22
Didymium	Di	48	Silver (Argentum)	Ag	108
Erbium	Er	?	Sodium (Natrium)	Na	23
Fluorine	F	19	Strontium	Sr	44
Glucinum	G	7	*Sulphur*	S	16
Gold (Aurum)	Au	197	Tellurium	Te	64
Hydrogen	H	1	Terbium	Tb	?
Ilmenium	Il		Thorium	Th	60
Iodine	I	126	Tin (Stannum)	Sn	59
Iridium	Ir	99	Titanium	Ti	24
Iron (Ferrum)	Fe	28	Tungsten (Wolfram)	W	92
Lanthanum	La	44	Uranium	U	60
Lead (Plumbum)	Pb	104	Vanadium	V	68
Lithium	Li	7	Yttrium	Y	32
Magnesium	Mg	12	Zinc	Zn	32
Manganese	Mn	28	Zirconium	Zr	34
Mercury (Hydrargyrum)	Hg	100			

The equivalent weights have here been placed in integers for reasons already assigned. The figures, it will be observed, have no relation to the solid, gaseous, or liquid form of the elements, or to their specific gravity; some substances widely different in chemical and physical properties have similar equivalent weights, while among others, a common difference may be observed. Thus lithium and glucinum are each represented by 7; aluminum and nitrogen by 14; cobalt and nickel by 30; iron and manganese by 28; and copper, zinc, yttrium, and phosphorus by 32. Lithium, sodium, and potassium, have a common difference of 16, these metals being respectively 7, 23, 39. The new alkaline metal, *Cæsium*, by its high equivalent (123) disturbs this order. Calcium, strontium, and barium, being strictly 20, 43·8, and 68·5, have nearly a common difference of 24. Other curious arithmetical relations may be found in chlorine, bromine, and iodine, as well as in other groups.

Equivalent Volumes.—In reference to elements and compounds which exist in the gaseous state, it has been determined by experiment that the weights correspond in general to very simple proportions by volume. Thus again taking *water* as an example, it is found that the proportion by volume in which hydrogen combines is always double that of oxygen; and further, that the compound formed, calculated as vapor, is exactly equal to the bulk of hydrogen which goes to constitute it. Assuming hydrogen as unity, by volume as well as by weight, it follows that the atomic weight of hydrogen (1) corresponds to the atomic volume 1; and that the above weight of oxygen (8) corresponds to 0·5, or one half volume. So in sulphuretted hydrogen 1 equivalent of hydrogen represents 1 volume, but the equivalent of sulphur (16) in consequence of the great specific gravity of the vapor of that element, corresponds to only 1-6th of the bulk of hydrogen, or 1-6th of a volume. This is the greatest deviation from simplicity among all the gaseous bodies; but its admission is unavoidable, except at greater inconvenience than arises from retaining it. Thus if, to avoid fractional parts of volumes, sulphur were made unity, *i. e.*, if 16 parts of sulphur by weight were assigned to 1 volume of the vapor, then the atomic volume of hydrogen would be 6, of oxygen 3, and of water 6. Some chemists have compromised this difficulty by avoiding the fraction for oxygen, but still retaining it for sulphur; although why, if retained for one, it should not be retained for both, does not clearly appear. Thus they represent 1 part by weight of hydrogen to correspond to 2 volumes of the gas, and 8 parts by weight of oxygen to 1 volume of that gas. They thus adopt hydrogen as unity by weight, but oxygen as unity by volume. Continental writers reject both of these arrangements; they take hydrogen at 12·5 by weight, and 100 by volume; oxygen at 100 by weight and 50 by volume.

Water, therefore, stands thus :—

	By Weight.		By Volume.		
Hydrogen	1	12·5	1	2	100
	or		or	or	
Oxygen	8	100·	$\frac{1}{2}$	1	50

It will be perceived that these numbers bear an exact ratio to each other. To us it appears desirable not to depart from the simplicity of ordinary chemical language, except for some cogent region. The atomic volume of hydrogen being 1, the atomic volumes of oxygen, phosphorus, and arsenic, are respectively $\frac{1}{2}$, and that of sulphur $\frac{1}{6}$th. With these exceptions there are no fractional volumes in the gaseous combinations of simple and compound bodies.

Gases or vapors which resemble hydrogen in containing one atom by weight in one volume are called *monatomic;* hydrogen, chlorine, and nitrogen, are examples. Those in which the volume corresponds to two atoms (oxygen, phosphorus, and arsenic) are called *diatomic*, and when the volume contains six atoms (sulphur), *hexatomic.*

Atomic Volume.—The atomic weight of a *gas* or vapor divided by the specific gravity (compared with *hydrogen*) will give the atomic volume. Thus the atomic weight of oxygen is 8 : bulk for bulk, it is 16 times heavier than hydrogen, and 8÷16=0·5, or $\frac{1}{2}$ the atomic volume of hydrogen. The atomic weight of sulphur is 16; compared with hydrogen in the same volume, its weight is 96 (the sp. gr. of its vapor at 900° being 6·63). Thus 16÷96=0·1666, or fractionally $\frac{1}{6}$th of a volume. If we take the ordinary specific gravity in which air is made the standard, the numbers for the atomic volumes of gases are in the same proportions. Thus hydrogen has a sp. gr. of 0 0691, and 1÷0·0691=14·4; oxygen, a sp. gr. of 1·1057, and 8÷1·1057=7·2; sulphur vapor at 900° a sp. gr. of 6·63, and 16÷6·63=2·41. These quotients 14·4, 7·2, and 2·41 are to each other as 1, $\frac{1}{2}$, and $\frac{1}{6}$th respectively, and they equally represent the atomic volumes of these bodies.

The atomic or equivalent volumes of all *solids* and *liquids*, whether elementary or compound, may be calculated on similar principles—namely, by dividing their atomic weights respectively, by their specific gravities compared with *water*, the atomic volume of which is $9 \div 1 = 9$. The sp. gr. of the metal lithium, the lightest of all solids and liquids is 0·59 : its atomic weight is 7, and $7 \div 0{\cdot}59 = 11{\cdot}8$, the atomic volume. Platinum, the heaviest of all solids, has a sp. gr. of 21·5, and its atomic weight is 99, and $99 \div 21{\cdot}5 = 4{\cdot}6$; the atomic volume of this metal. The atomic volume of ice, which, according to Playfair and Joule, has a sp. gr. of 0·9184, is found on a similar principle $\frac{9}{9184} = 9{\cdot}8$. The relative number of atoms in a given volume of any substance is obtained by an inverse proceeding—namely, in dividing the specific gravity by the atomic weight.

It appears probable from the researches of Petit and Dulong (*Ann. de Ch. et Phys.*, x. p. 403), that the atoms of all simple substances have the same *specific heat*, for by multiplying the specific heat of any one of the elements by its atomic weight, in nearly all cases the quotient is the same, or a multiple or sub-multiple of the figures. There are some remarkable exceptions, however, as in the case of carbon: and these can scarcely be explained by any want of accuracy, either in determining the specific heat or the atomic weights of bodies. Further researches are required to show that there is that exact relation which has been supposed.

New Notation.—A new system of notation has been proposed by Gerhardt, with a view to establish a constant relation between the atomic weight of bodies, their specific gravities, and vapor volumes. In order to carry out these views, he has suggested that hydrogen should be the standard or unit for the atomic weight, specific gravity, and combining volume, and that, in order to meet this view, the equivalents of certain bodies should be doubled. Thus:—

	Symbols.		Atomic Weights.
Hydrogen	H	H	1
Oxygen	$\underline{\mathrm{O}}$	*O*	16
Sulphur	S	*S*	32
Selenium	$\underline{\mathrm{Se}}$	*Se*	79
Tellurium	$\underline{\mathrm{Te}}$	*Te*	128·4
Carbon	$\underline{\mathrm{C}}$	*C*	12

The symbols are represented sometimes in Italic capitals, but more correctly in the Roman capitals barred, to show that they are double the usual weights. If this system be adopted, it will be desirable that this practice of barring the symbols should be maintained, otherwise endless confusion will arise in reference to the chemical constitution of bodies:—and the great object of a symbolic language in chemistry will be defeated.

The specific gravity of all gases is referred by Gerhardt to hydrogen as a standard, instead of atmospheric air. This certainly has the advantage of representing generally by one set of figures both specific gravities and atomic weights. Thus oxygen is 16 times heavier than hydrogen. Its specific gravity would be therefore 16, and, as it combines with hydrogen in the proportion of 8 to 1, this is in the ratio of 16 to 2; hence if the atomic weight of oxygen is 16, it will take two atoms of hydrogen to form water. Thus hydrogen is supposed to unite not as one, but as two atoms with one atom of oxygen, in order to meet this duplication of oxygen. This is on the assumption that equal volumes of gases, under similar circumstances, contain an equal number of atoms, and that each atom of an elementary gas represent a volume, and *vice versâ*. Thus a volume of oxygen contains 1 atom = 16, and a volume of hydrogen contains 1 atom = 1. But water, according to Gerhardt, cannot be produced by the union of 1 atom or volume of hydrogen; hence on his view it would stand thus:—

		By Weight.		By Volume.
H_2	=	2	=	2
$\underline{O}$	=	16	=	1
H_2O	=	18	=	2

Water would therefore be a suboxide of hydrogen, while the peroxide would become the oxide (HO). Protoxide of nitrogen would in like manner be a suboxide N_2O, and the deutoxide would become the protoxide (NO). While hydrochloric acid would remain unchanged (HCl), nitric acid would become NO_3H, and sulphuric acid SO_4H_2. Gerhardt's system would thus require not merely an entire change of formulæ, but an entirely new nomenclature, *i. e.*, if we are to preserve the rule of naming bodies according to their composition.

It is stated in favor of this method, that it is better adapted for expressing the formulæ of certain organic compounds than that now in use; and that, in reference to compound gases and vapors, the atoms may be so arranged that they will all yield two volumes—the specific gravities of the compounds, compared with hydrogen, being then equal to one-half of their atomic weights. Thus carbonic oxide $\underline{C\,O}$ forms 2 volumes of gas (the atoms being doubled); the atomic weight is 12+16, or 28, and the specific gravity, compared with hydrogen, equal to one-half, or 13.95. Alcohol is $\underline{C_2H_6O}$; it forms 2 volumes of vapor; the atomic weight is 24+6+16=46, and the specific gravity, compared with hydrogen, is one-half of this, namely, 23. Chemical facts are, however, somewhat strained to suit the requirements of this hypothesis. The specific gravities of arsenic and phosphorus in vapor, compared with hydrogen, are double their atomic weights, being 152·79 and 63·71 respectively. The atomic weights (75 and 32) therefore represent only half a volume instead of *one* volume of each element; and one volume of arsenic or phosphorus must represent two atoms. Either, therefore, the system is inconsistent with itself, and the assumption that the volume of an element represents one atom, or its atomic weight, is contrary to known facts—or, in order to bring arsenic and phosphorus within the rule, the atomic weights of these elements must be doubled on this system of notation. So with sulphur—the atomic weight being 32, the specific gravity of the vapor, compared with hydrogen, is 3 times this weight, or 96. Hence, instead of an atom of sulphur corresponding to one volume, it would be represented by $\frac{1}{3}$ of a volume. By ingeniously selecting a specific gravity of sulphur-vapor calculated for the unusual temperature of 1900°, in place of the ordinary specific gravity at 900°, this element is made apparently to fall within the rule. Oxygen itself only falls within it by doubling the equivalents of all the bodies with which this element combines.

This system, therefore, introduces duplicate or molecular atoms in place of the usual single atoms. Hydrogen does not exist as H, but as HH or H_2; in other words, it is a compound of itself, or a *hydride of hydrogen*, and nitrogen is also NN, or a nitride of nitrogen. We have here not only a departure from simplicity, but from all analogy. Thus we are told that anhydrous oxide of potassium is $\left.\begin{matrix}K\\K\end{matrix}\right\}\underline{O}$, while the anhydrous chloride, bromide, iodide, and fluoride, would be represented by one atom of each, KCl or KBr, &c. The analogy of composition between oxide and chloride is thus set aside: and the names of compounds are no longer in accordance with their chemical constitution. The reasons for the introduction of these material changes in the ordinary symbolic language of chemistry, are most unsatisfactory. The system of Gerhardt involves a series of unproved assumptions, and it requires a distortion of facts to square with these assumptions. The present language has been found adequate to explain all chemical changes that are of any importance and require explanation; and it has this great advantage, that it has now taken a deep root not only in the arts and manufactures of this country, but in medicine and pharmacy; and as a branch of scientific instruction, it should not be lightly changed. The system of notation suggested by Gerhardt has met with no support among French authorities. In the elaborate work on Chemistry by Pelouze and Fremy, now in course of publication, the ordinary method of notation is adopted.

Nomenclature. Constitution of Salts.—Elementary bodies often take their names from their peculiar physical properties, as chlorine and iodine in reference to color, and bromine to odor: in some instances the name is derived from the products of combination, as oxygen, hydrogen, nitrogen, and cyanogen. The general principle of nomenclature as applied to compounds, has been, as far as possible, to indicate the composition of the substance by the name. Thus sulphate of potash implies at once the constitution of this salt: it was formerly called the *sal de duobus.* Its formula is KO,SO_3, and herein its composition is at once announced. The same observation applies to other salts. In regard to the common metals, the salts receive the name of the metal, as sulphate of copper CuO,SO_3. The acid, however, as in the case of sulphate of potash, is believed to be combined with *oxide* of copper, and not with the metal itself. Among the alkalies the oxides were known long before the metals, and received specific names, which have been since retained. In recent times it has been proposed to assimilate the names of metallic salts, by using a common designation. Thus the sulphate of potash is described as sulphate of potassium, on the hypothesis that the acids are not combined directly with the oxides, but with the metals. If, as we believe, this hypothesis is inconsistent with chemical facts, then a retrograde step in nomenclature has been taken, since a name which suggests a direct combination of an acid or acid radical with a metal, conveys an incorrect idea of the constitution of salts. (*See* p. 68.)

A *salt* is a compound of an acid and a base. An *acid* is a compound which has an acid or sour taste, which reddens the blue color of litmus, and neutralizes an alkali in combining with it to form a salt. The term *base* is applied by chemists to signify a compound which will chemically combine with an acid: it includes alkalies (oxides of alkaline metals, and alkalies of the organic kingdom), oxides of the ordinary metals, and a variety of complex compounds in the organic kingdom which are not alkaline and possess none of the characters of metallic oxides. The metals which form bases are now called basylous bodies. An *alkali* is known by its having an acrid or caustic taste, by its rendering a red solution of litmus blue, and by its being *neutralized* by an acid, *i. e.*, having its alkaline properties entirely destroyed. Further, it has the property of turning yellow turmeric to a red-brown color; the red color of the petals of flowers, and fruits, to a blue or green; and the red color of woods and roots to a crimson tint. The basic metallic *oxides* are generally insoluble in water, and neutral to test-paper; some have a feebly alkaline reaction.

In reference to *Oxacids*, or those which contain oxygen, the termination *ic* indicates the higher degree of oxidation, while the termination *ous* implies a lower degree. Thus we have sulphuric (SO_3) and sulphurous (SO_2) acids. When there are more than two acids, a further distinction is made by the prefix *hypo* (ὑπὸ under): thus we have hyposulphuric acid to signify an acid containing a smaller quantity of oxygen than the sulphuric, but a larger quantity than the sulphurous; and hyposulphurous, indicating a smaller quantity of oxygen than exists in the sulphurous acid. When an acid has been discovered containing a still larger amount of oxygen than the highest in a known series, it receives the prefix *hyper* (ὑπὲρ above); still retaining the terminal *ic*. Thus there is manganic acid (MnO_3); and hypermanganic or permanganic acid (Mn_2O_7), which contains a still larger proportion of oxygen than the manganic. The salts formed by these acids terminate in *ate* when the acid terminates in *ic*, and in *ite* when it terminates in *ous*. The terminations *ic* and *ous* have been employed by Berzelius, and other chemists, to distinguish the oxides and salts of metals. Thus the protoxide of iron would be the ferrous oxide, while the peroxide would be the ferric oxide; so there are also ferrous and ferric sulphates—stannous and stannic chlorides and sulphides.

When there is only one acid formed by the same elements, its termination is always in *ic*, as the boracic acid, formed of boron and oxygen, of which only one compound is known. The class of *hydracids* includes those binary compounds in which hydrogen is a constituent; and the names imply at once the composition as hydrochloric acid (HCl). Hydrogen, unlike oxygen, does not form more than one compound with the same element or *radical*. These hydrogen acids require no water for the manifestation of acidity. The term radical, or *compound radical*, is applied to a compound which in its order of combination acts like an element. Thus the compound gas cyanogen (C_2N) is a radical; it enters into combination with the metals and metalloids, like chlorine, producing binary compounds called cyanides. It is a substitute for an element.

When in the composition of salts the atoms of acids preponderate, the prefix *bi* or *ter* is used to indicate the number, as bisulphate of potash ($KO2SO_3$), or tersulphate of alumina ($Al_2O_3 3SO_3$). These constitute acid salts. When the base predominates, the abbreviated Greek prefix *di* or *tri* is employed to designate the surplus atoms of the base. Thus, the triacetate of lead signifies a compound in which three atoms of oxide of lead are united to one atom of acid $3(PbO)\overline{Ac}$. The term *sesqui* is used to signify one and a half atoms, or, avoiding fractions, 3 atoms of base to 2 of acid as $3PbO,2\overline{Ac}$. The following Table represents the nomenclature of salts in reference to their constitution. M stands for any metal:—

Neutral (normal) salt	$MO, + SO_3$	Bibasic	$2MO, + SO_3$
Acid	$MO, + 2SO_3$	Sesquibasic . .	$3MO, + 2SO_3$
Sesquisalt	$2MO, + 3SO_3$	Tribasic . . .	$3MO, + SO_3$

Binary Compounds,—The Binary System.—When a metalloid is united to another metalloid or metal, or when a compound radical (salt-radical) is united to a metal or metalloid, the combination is called *binary*, from its consisting of two elements. They are generally known by the termination *ide*. Thus oxide, chloride, sulphide, carbide, phosphide, and cyanide indicate compounds of the elements or of the radical (cyanogen) with other elements. When more than one combination exists, the compounds take the Greek prefix *proto*, *deuto*, *trito*, or *di*, to indicate the respective number of atoms of the constituents. (*See* OXYGEN for the series of *Oxides.*) The highest combination always takes the prefix *per*. The binary compounds formed by chlorine, bromine, iodine, and fluorine, with the alkaline metals, are frequently called *haloid* salts, to indicate the marine origin of the radicals (ἅλς, ἁλὸς, the sea).

Chloride of sodium furnishes an instance of a binary compound; and as nitrate of silver or nitrate of potash equally forms a salt bearing a physical resemblance to the chloride, it has been suggested that in oxacid salts the elements may be so arranged as to form hypothetical binary compounds. Chloride of sodium is $NaCl$ and nitrate of silver is AgO,NO_5; but the accepted symbolic language would admit of the atomic arrangement $AgNO_6$, and by this means all decompositions would become mere substitutions of one metal for another, or for hydrogen. Thus in the production of chloride of silver, we should have in ordinary symbols $NaCl+AgO,NO_5=AgCl+NaO,NO_5$; but if the oxygen is supposed to be associated with the elements of nitric acid, forming a compound radical (nitrion), then the changes would be more simply represented thus: $NaCl+AgNO_6=AgCl+NaNO_6$. If, however, this view were correct, it should apply to all salts and even to hydrates. Thus, to take a few examples of compounds which are intelligibly represented by the present method, we should have, on the binary hypothesis, to make the following changes: 1. Carbonate of soda, as a type of the carbonates, NaO,CO_2 would be rendered Na,CO_3; and for the bicarbonate of soda, $NaO,2CO_2$ a new hypothetical radical would have to be created, as Na,C_2O_5 or Na,CO_3+CO_2, neither of which formulæ would convey the slightest knowledge of the composition of the salts. This objection equally applies to all salts having one atom of base to two or more atoms of acid, as the bisulphates, bisulphites, the binarsenates, and others, as well as to all double salts containing an oxygen acid. 2. In the application of this notation to hydrates (which could not be fairly excepted), hydrate of potash KO,HO would be K,HO_2; but while potassium (K) has a stronger affinity for oxygen than any other known substance, and peroxide of hydrogen (HO_2) so readily parts with oxygen that the mere contact with metals or metallic oxides is sufficient for the purpose, it is assumed that the peroxide can remain in combination with potassium without undergoing decomposition. 3. Sulphurous acid by combining with potash forms KO,SO_2. It could not be regarded or written as KSO_3, for this would imply a combination of anhydrous sulphuric acid with the metal potassium. The bisulphite of potash $KO,2SO_2$, would present an equal difficulty. On the binary system this would be K,S_2O_5—the sulphur and oxygen, in order to form a salt radical, being here associated as in hyposulphuric acid, which is a well-known and independent acid of sulphur. 4. The anhydrous salts formed of metallic bases and acids could not be consistently represented on the binary hypothesis; for there could be no definite principle on which the oxygen should be *wholly* assigned to either metal. Thus chromate of lead is commonly represented as PbO,CrO_3, but as a binary compound it would be either Pb,CrO_4, or $CrPbO_4$. Of these three combinations of elements, those only which are known and separable, are oxide of lead and chromic acid. The necessary creation of an endless number of hypothetical radicals, some already conflicting with known compounds, is indeed fatal to the hypothesis. It would add complexity instead of simplicity to chemical formulæ. While NO_5, SO_3 and CO_2 have a real and independent existence, the binary radicals NO_6, SO_4 and CO_3 are mere assumptions. It has been supposed that the electrolytic decomposition of salts is in favor of this view; but although the metal may be separated from the salt by an electric current, the supposed binary radical has never been obtained, and the facts are fully explained on the supposition that it is SO_3+O, and not SO_4. On the other hand, ordinary electrolysis favors the common view of the constitution of salts by acid and base, as the following simple experiment will show. Provide a piece of glass tube, bent at an angle, and placed in a wine-glass, to serve for its foot or support. Fill this syphon with the blue infusion obtained by macerating the leaves of the red cabbage in boiling water (rendered blue by a little potash), and put into it a few crystals of sulphate of soda; then place a strip of platinum foil in each leg of the syphon, taking care that they do not come into contact at the elbow of the tube, and connect one of these with the negative and the other with the positive pole of the pile; in a few minutes the blue color will be changed to green on the negative side, and to red on the positive side of the tube, indicating the decomposition of the salt, the alkali or soda of which is collected in the negative, and the sulphuric acid in the positive side. Reverse the poles, and the colors will also gradually be reversed. In this and analogous experiments, it is found that, whenever a neutral salt is decomposed by electricity, the oxide or base appears at the cathode, and the acid at the anode. The bases, therefore, in their electrical relations, rank with hydrogen, and are cathïons; and the acids with oxygen, and are anïons (*see* page 56). The most difficultly soluble salts may be made to render up their elements in the same way. If, for instance, we substitute for the sulphate of soda in the preceding experiment, a little finely-powdered sulphate of baryta moistened with water, baryta will be evolved at the cathode, and will there render the liquor green; while sulphuric acid will appear at the anode, rendering it red.

If the binary hypothesis were adopted, it would be necessary to change the names of all salts. CO_3 is not carbonic acid; it would be necessary to invent a new term for this radical, to indicate its composition, *e.g.*, a teroxycarbide, so that dry carbonate of potash KO,CO_2, would be a teroxycarbide of potassium KCO_3. If names are not to express, as far as may be, the composition of salts, it would be preferable to return to the old nomenclature based on physical properties, and to designate the sulphate of iron (FeO,SO_3) as green vitriol, rather than under the binary hypothesis as the tessaroxisulphide of iron ($FeSO_4$). We must bear in mind, in reference to such changes, that the supposed advantages gained in one part of the science may be far more than counterbalanced by the disadvantage of using names which either do not express the nature of the compound, or which express it in such formulæ as to deceive the student of the science. As Dr. Miller has pointed out, there are four ways in which nitrate of potash may be represented; KO,NO_5; K,NO_6; KNO_6; and KNO_3; but to only the first of these is the usual name of the salt applicable. The first, second, and third formulæ are on the ordinary system of notation; the fourth is on the system of Gerhardt, which, except by some conventional understanding, cannot represent the presence of potash or nitric acid in the salt on any reasonable interpretation.

There are some cases in which the binary theory of salts is inadmissible not only with respect to oxacids, but to hydracids. The alkalies of the vegetable kingdom form definite crystallizable salts with the hydrochloric, sulphuric, and nitric acids. The hydrochlorate and sulphate of morphia are well-defined salts, in which there is every reason to believe that *acid* and *base* are directly combined. Even in the mineral kingdom, there is sometimes a want of evidence of this binary condition. Magnesia or alumina may be dissolved in hydrochloric acid, and it is supposed that soluble chlorides are formed. In the case of soda and potash there is the strongest evidence of the production of chlorides by the fact that the binary salts are obtainable as such by crystallization. On submitting to evaporation the hydrochloric solutions of magnesia and alumina and applying heat to the dry residues, no binary compounds are obtained, but simply the bases which were originally employed. According to some authorities, cobalt forms both a chloride and hydrochlorate, indicated by a different color in the compounds; the chloride or binary compound obtained by concentration at a high temperature being blue, while the hydrochlorate, like the non-binary compounds nitrate and sulphate, although deprived of water, remain red.

Neutralization, in reference to salts, must be distinguished from *saturation*: the first implies the destruction of the properties of acid and alkali by combination, as manifested on organic colors; the second the exhaustion of chemical affinity. Potash is neutralized by combination with one atom of sulphuric acid. The compound, sulphate of potash, presents neither acid nor alkaline reaction; it is a perfectly neutral salt. Potash will however combine with an additional equivalent of acid, forming a bisulphate; in this compound it is saturated with the acid, but the alkali is more than neutralized; it possesses a well-marked acid reaction. Potash in the state of bicarbonate is saturated with carbonic acid; it will take no more: but it is not neutralized, for it presents a well-marked alkaline reaction. These terms are often used as synonymous, but they have a widely different signification. The term *neutral* salt is however commonly employed to signify the condition of a compound without reference to the action of its solution on vegetable colors. Provided the same equivalent weight of acid is present, the salt is neutral although the solution may have an acid reaction. The sulphates of copper, iron, and zinc contain the same proportion of acid to base as the sulphate of potash, but while the latter is quite neutral, the three former are acid, and redden litmus. The best test for neutrality is the blue infusion of cabbage, prepared in the manner elsewhere described (page 69). It is reddened by an acid, and changed to a green color by an alkali. To avoid confusion from the use of the term neutral, Gmelin has proposed to call such salts *normal.*

In the double decomposition of salts it is usual to state that neutral salts produce neutral compounds. This may be proved by adding to solutions of sulphate of potash and chloride of barium respectively a small quantity of blue infusion of cabbage. When mixed, there is a complete interchange of acids and bases, but the mixed liquids remain blue. Hence there must have been a complete substitution or replacement of acids and bases in equivalent proportions; in other words, the chloride of potassium and sulphate of baryta are just as neutral as the compounds which form them. If an equivalent of bisulphate of potash is employed, the blue liquid will be reddened by this salt, and remain red after mixture, an equivalent of hydrochloric acid being set free. When solutions of phosphates of soda and chloride of calcium, colored with blue litmus, are mixed, the compounds, although neutral, so decompose each other as to set free an acid, and the litmus is reddened. This is owing to the formation of a basic phosphate of lime, *i. e.*, a salt in which the base predominates. An acid and an alkaline salt may by double decomposition produce neutral compounds. A solution of alum reddened by infusion of litmus or blue cabbage, when mixed with a due proportion of a solution of carbonate of potash rendered green by infusion of cabbage, will give rise to products of a neutral kind (sulphate of potash and hydrate of alumina), and both liquids will become blue.

METALLOIDS OR NON-METALLIC BODIES.

CHAPTER V.

METALLOIDS AND METALS.—PROPERTIES OF GASES AND VAPORS.

Division of Elements.—For the convenience of study, elementary bodies are divided into two great classes, namely, METALLOIDS and METALS. This division is arbitrary; hence chemists have taken different views of the substances which belong to these two classes. Sulphur may be regarded as a type of the metalloids, and gold of the metals. Here the distinctions in physical characters are sufficiently marked. In some cases, however, it is difficult to assign the class; thus arsenic, tellurium, and selenium have been regarded either as metallic or non-metallic. It is difficult to suggest any broad chemical distinction between the two classes. As a general rule, non-metallic bodies produce, in combining with oxygen, either acids or neutral oxides; they do not form any salifiable base. Water may be regarded as an exception to the remark: since, although a neutral oxide, it is believed by most chemists to act, in some instances, the part of a base to acids, and is known as basic water. Hydrogen therefore ranks with the metals as a basylous body, and takes the first place as an electro-positive. On the other hand, the metals, while they produce acids in combining with oxygen, also produce alkalies, earths, and oxides; in fact, they are the chief source of the bases from which salts are formed.

English writers commonly enumerate as non-metallic 13 out of the 65 elementary bodies known to science. They comprise 4 gaseous, 1 liquid, and 7 solids, with 1 the physical state of which is unknown. They are contained in the subjoined list:—

OXYGEN	gaseous.	BROMINE (liquid)		PHOSPHORUS	solid.
HYDROGEN		FLUORINE (unknown)		CARBON	
NITROGEN		IODINE	solid.	BORON	
CHLORINE		SULPHUR		SILICON	
		SELENIUM			

The symbols and atomic weights of these bodies will be found at page 63.

Distinction of Gases and Vapors.—The gaseous, liquid, or solid state, is well known to be a physical condition of matter, depending on the heat associated with the atoms of the solid or liquid. By heating a solid, we may cause it to pass through the liquid and vaporous conditions. Thus camphor placed in a retort and heated to 347° melts or passes to the liquid state. If the temperature be raised to about 400°, it is rapidly converted into a transparent vapor or gas, which is deposited in white flocculent masses on all cold surfaces. Thus distilled from a short retort into a long jar placed upright, it forms a beautiful illustration of the solidification of a vapor by cooling. Ether is, at ordinary temperatures, a liquid: if cooled to about —24° it becomes a solid like camphor; but if the liquid be heated to 96°, it is entirely converted to vapor or gas, having at and above this temperature all the physical properties of a gas. The best method of proving this is to invert in a wide dish of water, heated to above 100°, a small gas-jar filled with water at this temperature. If a tube containing liquid ether be opened under the mouth of the jar in the hot water, the ether will pass into the vessel as gas or vapor, and displace the water. The jar may be removed, and the contents inflamed by a lighted taper, when it will be seen to burn like coal-gas. If another jar be similarly filled with the vapor, and transferred to a basin of cold water, or if cold water be simply poured over it, the gaseous contents will be condensed, the ether will be liquefied, and the cold water will rise and fill the jar.

Liquefaction of Gases.—Experiments conducted on these principles led Mr. Faraday to the remarkable discovery that a large number of gases are merely the vapors of liquids or solids. It is a well-known fact, that when any gas is submitted to sudden and violent pressure, great heat is given out. A small volume of air, suddenly compressed, evolves so much heat as to ignite inflammable substances. Thus a piece of amadou, or German tinder, may be kindled by the sudden compression of a few cubic inches of air in a dry and warm glass cylinder. If, therefore, a gas is submitted to pressure, and at the same time cooled as it is compressed, the conditions are such as to cause it to pass into the liquid state.

With some gases no pressure is necessary—mere cooling will be found sufficient. Sulphurous acid is a gaseous body, at all temperatures above 14°. When cooled to this temperature, it is immediately liquefied. If sulphurous acid gas in a dry state be passed through a tube immersed in a freezing-mixture of pounded ice and salt, it will be condensed as a liquid in the bend of the tube, and if the horizontal portions be drawn out in a capillary form in the first instance, the liquefied gas, when condensed, may be sealed up and preserved. If the tube be broken, the liquid will rapidly pass to the gaseous state, producing a great degree of cold. Under sufficient pressure, the amount of which varies with each gas, some of these bodies may be liquefied without cooling, and the pressure may be produced by the gas itself.

The solid crystalline hydrate of chlorine ($Cl+10HO$) inclosed in a stout bent tube sealed, yields, when gently heated, chlorine liquefied by its own pressure, forming about one-fourth of the liquid obtained in the cool part of the bent tube. The liquefaction of ammonia may be performed in like manner, by saturating dry chloride of silver with the gas, and introducing this into a stout glass tube bent at an obtuse angle and securely sealed. The ammonio-chloride of silver melts at about 100°. The ammonia is evolved, and may be condensed to a liquid by cooling the other end of the tube. The ammonia is reabsorbed by the chloride on cooling, so that this experiment may be repeated any number of times (Mitscherlich). If a substance like cyanide of mercury, capable of yielding ten cubic inches of gas, is inclosed in a stout tube of one cubic inch capacity, the gas, when evolved, will be under a pressure of ten atmospheres (15×10), or 150 pounds on the square inch, a pressure quite sufficient to make it assume the liquid state. Faraday thus condensed many of the gases by merely exposing them to the pressure of their own atmospheres. He placed the materials for producing them in strong glass tubes, a little bent in the middle, and hermetically sealed. Heat was then applied to the substance; and when the pressure within became sufficient, the liquefied gas made its appearance in the empty end of the tube, which was artificially cooled to assist in the condensation. In these experiments much danger may be incurred from the occasional bursting of the tubes; so that the operator should protect his face by a mask, and his hands by thick gloves. The greatest caution should be always observed in performing the experiment. Faraday succeeded in liquefying the following gases, which, as will be seen, required various degrees of pressure for the purpose.

	Pressure in Atmospheres.		Fahr.		Pressure in Atmospheres.		Fahr.
Sulphurous acid . . .	2	at	45°	Sulphuretted hydrogen .	17	at	50°
Chlorine	4	"	60	Carbonic acid	36	"	32
Cyanogen	4	"	60	Hydrochloric acid. . .	40	"	50
Ammonia	6·5	"	40	Nitrous oxide	50	"	45

Faraday subsequently succeeded in liquefying olefiant gas and fluosilicic acid, and in solidifying hydriodic and hydrobromic acid gases, oxide of chlorine, and protoxide of nitrogen (*Phil. Trans.*, 1823 and 1845; also Bunsen, *Bibliothèque Universelle*, 1839, vol. 32, p. 105; and Poggend. *Ann.*, vol. 12, p. 132).

By employing a bath of solid carbonic acid and ether, Faraday produced a degree of cold amounting to —106° in the open air, and —166° *in vacuo*. By exposure to a cold of —106° without pressure, the following gases were liquefied:—

Chlorine.
Cyanogen.
Ammonia.
Sulphuretted Hydrogen.
Hydriodic acid.
Hydrobromic acid.
Carbonic acid.
Oxide of chlorine.

With the aid of powerful condensing pumps, and a cold of —166°, all the gases excepting six were liquefied, and those above-mentioned were solidified, as well as the protoxide of nitrogen. Carbonic acid is, however, readily obtained in the solid state as the result of the cold produced by the sudden escape of its own vapor. The six which resisted liquefaction at this low temperature, and under a pressure varying from 500 to 750 pounds on the square inch, were the following:—

Oxygen.
Hydrogen.
Nitrogen.
Carbonic oxide.
Deutoxide of nitrogen.
Coal-gas.

It will be perceived that of these, three are simple and three are compound gases. In employing a mixture *in vacuo* of liquid protoxide of nitrogen and sulphide of carbon, Natterer succeeded in producing a degree of cold equal to —220°, but without any effect upon these six gases. Dr. Andrews reported to the British Association (Sept. 1861), that by pressure alone he had succeeded in reducing oxygen to 1-324th of its volume, and by pressure with a cold of —106°, to 1-554th of its volume; and atmospheric air by pressure and cold to 1-675th, in which state its density was little inferior to that of water (the difference between air and water at 60° being 814.) Hydrogen was condensed by similar means to 1-500th, carbonic oxide to 1-278th, and deutoxide of nitrogen to 1-680th. The gases were compressed in the capillary ends of thick glass-tubes, so that any physical change they might undergo, could be easily observed. When thus highly condensed, they were not liquefied; hence, although these six gases are probably the vapors of liquids, they must be regarded at present as *permanent gases*, since cold and pressure conjoined, and carried to the utmost limits, do not cause them to assume the liquid condition.

From these facts, we learn that the greater number of gases, simple and compound, are the *vapors* of liquids and solids. They differ from ordinary vapors simply in the fact, that the boiling points of their liquids are far below the ordinary temperature of the atmosphere ; hence they only admit of condensation by artificial cooling. A true vapor, like that of ether, is condensed on its production, because the temperature of the air is below its boiling-point, 96° : it requires no artificial cooling for its condensation. In any part of the earth in which the temperature was 96°, ether would be a permanent gas, unless kept under pressure; while in any part where the temperature did not exceed 14°, sulphurous acid gas would always exist as a liquid. The difference between vapors and gases is therefore merely a physical difference dependent on temperature. A gas is permanently that which a vapor is temporarily.

The sulphide of carbon as a liquid is stated to resist a very low degree of cold without solidifying. The intense cold produced by its evaporation is, however, sufficient to bring the evaporating liquid to the solid state. Pour a small quantity of sulphide of carbon into a watch-glass. Place a few fibres of asbestos on a slip of filtering paper, so that one end may be immersed in the liquid, and the other passed freely over the edge of the glass. In a few minutes the projecting end will be fringed with a snow-like deposit of a solidified vapor. This may serve as an illustration of the cooling process by which solid is obtained from liquid carbonic acid.

The laws which govern gases also govern vapors, so long as they have a temperature above the boiling-points of their respective liquids.

Physical Properties of Gases and Vapors.—Gases have no cohesion. Their volume is determined by the capacity of the containing vessel ; and it is remarkably affected by slight changes in temperature and pressure. (The rules for calculating changes in volume from these causes will be found in the APPENDIX). Unless gases are confined within a closed space, as in caoutchouc or bladder, or in a gas-jar inverted in water, we can have no knowledge of their materiality, or of the fact that they exclude other bodies from the space which they occupy. When secured in membranes, they manifest remarkable elasticity ; they are easily compressed into a smaller bulk, but immediately resume their original volume on the removal of the pressure. They gravitate, and therefore have weight ; but as they are light compared with their bulk, their weights are generally given for 100 cubic inches (nearly one-third of a gallon). Owing to their great elasticity, their volume is affected by the height of the column of liquid in which they are standing, as well as by the density of the liquid itself. Thus a gas admits only of accurate measurement in a graduated vessel, when the liquid on the outside of the jar is precisely on a level with the liquid on the inside. If the level in the inside be higher, the gas is under diminished pressure from the gravitating force of the column of liquid ; and the contents of the graduated jar, as read off in cubic inches, appear greater than they really are. If by pressing the vessel downwards, the level on the inside is below that on the outside, the gas is under increased pressure, and the contents are less than they appear to be. The substitution of water for mercury makes a considerable difference in the volume of a gas. Fill a long stout tube with mercury, and invert it in a basin containing just enough mercury for this purpose. Allow two or three cubic inches of air to pass up the tube, and then mark the level of the mercury. Now pour into the basin, water colored with litmus, or indigo, and then raise the tube into the colored water, so that the mercury may flow out. As it flows out, the water takes its place, and it will be found when the substitution is complete, that the gas now has only from one-third to one-half of the volume which it had when over the mercury. The inside column of mercury gravitates with more force than that of water, and the expansibility of the gas allows it to occupy a larger space. Over water the gas contracts nearly to its proper bulk.

The following experiments will illustrate the effects of atmospheric *pressure* on the volume of gases. Tie securely a piece of thin caoutchouc over the mouth of a wide short jar. Place it under a receiver on the air-pump plate, and exhaust the vessel. As the pressure of the air is removed from the interior, that which is contained in the vessel expands and raises the caoutchouc considerably. This phenomenon disappears on letting the air pass into the receiver.—Adjust a small bladder with a leaden weight, so that it will just sink, in a tall jar of water. Place this under a receiver, as in the preceding experiment, and withdraw the air. The air in the bladder expands by removal of pressure from the surface of the water, and the bladder instantly rises to the surface, by reason of the increased volume of its contents. On letting in the air, it again falls to the bottom of the vessel.—The effect of *heat* may be shown by various experiments. Invert a long tube, having a thin bulb, of about three inches' diameter, at one end, the other, or open end, being immersed in a solution of litmus contained in a bottle. Heat the bulb by a spirit-lamp to expel some of the air, when, on cooling, the colored liquid will rise to one-third or one-half the height of the tube. This will now serve as a delicate air-thermometer. On applying the warm hand to the bulb, the increase in the volume of air will be at once perceptible by the descent of the colored liquid in the tube; and the contraction or diminution of volume by cold may be shown by pouring a little ether over the bulb. The cold produced by the evaporation of this liquid, condenses the contained air, and the colored liquid rises in the tube.—Heated air, by reason of the increase of volume, is lighter than cold air. Balance on a scale-beam a thin glass shade of some capacity, with the open end downwards. Place a spirit-lamp under the shade; the increase in volume and diminution of weight in the heated air are at once manifested by the rising of the shade. Again, a small bladder so balanced with lead as just to sink in cold water, will, by the expansion of air in the bladder, rise to the surface if placed in a jar of hot water.

Pressure and temperature, within very slight limits, affect all gases equally, whether compound or simple, however they may differ from each other in density. There is, however, a peculiarity in the expansion of gases by heat, whereby they are distinguished from liquids. The same quantity of heat will expand a gas, in an equal degree, at a high and a low temperature; but with liquids the expansion is, for the same quantity of heat, proportionably greater at high than at low temperatures.

It has been ascertained by Dalton and Gay-Lussac that 1000 measures of dry air, when heated from the freezing to the boiling point of water, undergo an increase in bulk about equal to 375 parts; so that 1000 cubic feet of air at 32° become dilated to 1375 cubic feet at 212°. Air, therefore, at the freezing-point expands $\frac{1}{480}$th part of its bulk for every added degree of heat on Fahrenheit's scale (for $375 \div 180 = 2{\cdot}08$, and $1000 \div 2{\cdot}08 = 480$). Hence, assuming that the volume of air is 480 cubic inches, thus,

480 cubic inches, at 32°, become
481 " at 33°,
482 " at 34°, &c.

increasing one cubic inch for every degree. A contraction of one cubic inch occurs for every degree below 32°: thus,

480 cubic inches, at 32°, become
479 " at 31°,
478 " at 30°, &c.

The volume of air, therefore, at 32° would be doubled at 480°, and tripled at 960°: the latter temperature being about that of a dull red heat. Steam, and all other vapors, when heated out of contact of their respective fluids, are subject to laws of expansion similar to those of air. It may be remarked, in regard to the expansion sustained by gases as a result of increase of temperature, that, although great in amount, the actual force which is thus exerted is small (when compared with that of solids and liquids under the same circumstances), in consequence of their extreme elasticity: thus, although the volume of air (or of vapor) is about tripled by red heat, vessels easily sustain the pressure.

(For the determination of the increase and decrease of volume as a result of changes of temperature, *see* APPENDIX.)

Incandescence.—It is a remarkable fact, that gases which appear of such an attenuated nature, can, even when brought almost to a state of vacuum, be rendered incandescent by the high temperature of the electric spark. No oxygen is present, therefore there can be no combustion. Hydrogen, nitrogen, sulphurous acid, and other gases, inclosed in tubes through which the electric spark from Ruhmkorff's apparatus is discharged, evolve an intense light as the result of incandescence; and this light not only presents a different color for each gas in its vacuous state, but it is resolvable into a spectrum of colored bands of different degrees of refrangibility. Thus when pure hydrogen is placed in a tube, which is afterwards brought almost to a state of *vacuum* by an air-pump, it is found that under a discharge from the coil, a fine ruby red light is evolved; while the nitrogen vacuum, under similar circumstances, gives a magnificent violet light (MILLER). The spectra produced by the lights of these gases are singularly contrasted; while the nitrogen spectrum includes rays of high refrangibility, that of hydrogen contains only rays of low refrangibility, and these have scarcely any action on the collodio-iodide of silver.

Specific Gravity.—Density.—Gases and vapors vary in specific gravity. As a general rule, the air is taken as a standard, and all gases are compared with it under similar circumstances of temperature, pressure, humidity, dryness, &c. The lightest of all gases is hydrogen, which is 14·4 times lighter than air. Among the heaviest is the vapor of iodine, which is, bulk for bulk, nearly 9 times as heavy as air. The greater number of simple and compound gases are of about the same weight as air, or a little heavier. (The rules for calculating the specific gravity of gases and vapors will be found in the APPENDIX.) It has been proposed to substitute hydrogen as a standard of comparison instead of the atmosphere, because it is the lightest of the gases, and it will place the equivalent weights and specific gravities of these bodies, with few exceptions, in a uniform relation; but we do not take naphtha as the standard for the specific gravity of liquids, nor lithium as the standard for solids; and the selection of air for gases, and of water for liquids and solids, has been so confirmed by long use, that any change would be attended with great inconvenience. A volume of air may be obtained for the purpose of weighing, with much greater certainty than a volume of pure hydrogen, not to mention that for equal weights nearly fifteen times as much hydrogen as air must be taken in one experiment—thus increasing the chances of error. Gerhardt and others, who have advocated this change to suit an hypothesis, have entirely forgotten that if the standard is changed for specific gravity, it will entail a change for specific heat, the refractive power of gases, the law of diffusion, &c., in reference to which, air is now universally taken as a standard.

Specific Heat.—By this it is to be understood the proportional quantity of heat contained in equal *weights* of different gases at the same thermometric temperature. The absolute quantity of heat contained in two gases, as well as in two liquids, at the same temperature, is very different. A thermometer, in fact, can only show the relative quantity present. Gases are equally expanded or increased in volume by equal additions of heat; but unequal quantities of heat will be required to raise them to the same degree; and for this reason unequal quantities will be given out by them in cooling from a high to a low temperature.

When equal weights of different gases, heated at 212°, are passed slowly through a glass tube immersed in cold water, the temperature of the water is raised while the gas is cooled. The relative heating power of gases has been thus measured and tabulated—atmospheric air being taken as the standard of comparison:—

Hydrogen	12340	Air	1000
Olefiant gas	1576	Protoxide of Nitrogen	887
Carbonic oxide	1080	Oxygen	884
Nitrogen	1031	Carbonic acid	828

These figures represent the specific heat or the capacity for heat of different gases. As each compound gas has its own specific heat, without reference to the specific heats of its constituents, it follows that this physical property of gases, may be occasionally applied to distinguish a gaseous chemical compound from a gaseous mixture. It has been thus applied to the constituents of the atmosphere.

Light.—Gases exert a refracting power on light peculiar to each, and the refracting power of a compound gas is not equal to the mean refracting powers of its constituents. The refracting powers of the subjoined gases have been determined by Biot and Arago, and are as follows:—air being the standard.

Hydrogen	6614	Nitrogen	1034
Ammonia	2168	Carbonic acid	1004
Carburetted hydrogen	2092	Air	1000
Hydrochloric acid	1196	Oxygen	861

Hydrogen has the highest and oxygen the lowest refracting power among these gases.

Light, like the electric fluid or heat, has in some instances a combining power over gases. Thus a mixture of chlorine and hydrogen is converted to hydrochloric acid with explosion, when exposed to the direct rays of the sun or any intense light, as the oxyhydrogen or lime light; but more slowly and gradually in diffused light, such as daylight. Bunsen and Roscoe have ingeniously made the rate of combination a measure of the intensity of light for photometrical purposes, and have thus been able to institute numerous comparisons on the relative intensities of artificial lights and the light of the sun. This combining power resides in those rays of the spectrum which are near to the more refrangible colors, the violet and blue; although not visible in the ordinary spectrum, they may be made visible by uranium glass. When exposed to the yellow, orange, or red rays, the two gases show no tendency to combine. This is in accordance with the action of light on the salts of silver.

Magnetism.—Faraday has discovered that there is a difference among gases, as to their magnetic properties, when secured in glass tubes and delicately suspended in the field of a powerful artificial magnet. Of the following gases, four were found to be magnetic, taking up a north and south position (axial) like the common magnet; while three were diamagnetic, taking up a position at right angles, or east and west (equatorial). In measuring the intensity of this power, it was found that a vacuum in the glass tube was 0·0, and that oxygen manifested the greatest magnetic force. The following Table represents the relative intensities:—

Oxygen	17·5	magnetic.	Carbonic acid	0·0	
Air	3·4		Hydrogen	0·1	dia-magnetic.
Olefiant gas	0·6		Ammonia	0·5	
Nitrogen	0·3		Cyanogen	0·9	

A Vacuum, 0·0.

[The reader will find in the APPENDIX a Table of the principal gases and vapors and their compounds, representing in a concise form their combining volumes, atomic weights, specific gravity, and the weight of 100 cubic inches.]

Diffusion.—There is a property of gases which is known under the name of *diffusion.* This implies a power by which they intermingle with each other in spite of a difference in specific gravity, and when they have no tendency to combine chemically. If we half fill a bottle with mercury, and pour upon this, ether—it is well known that the two liquids do not combine chemically, and that there is a great difference in their specific gravities. Hence, it is hardly necessary to observe, that however long these liquids may be in contact in a closed bottle, the mercury will not rise into the ether, nor will the ether descend into the mercury. Further, if shaken together and thus mixed, they will in a few minutes be completely separated according to their specific gravities. Carbonic acid and hydrogen among gases have no tendency to form a chemical union, and they differ more from each other in specific gravity than mercury does from ether. Invert a jar, well-ground, containing hydrogen, on a similar jar which it will accurately fit, placed below—containing carbonic acid. After from five to ten minutes' contact at the ordinary temperature, carbonic acid will be found in the upper jar (by the appropriate test, lime-water), and hydrogen will be found in the lower (by the application of a lighted taper and the combustion of the gas). If this experiment is performed in bottles, it will be found that the two gases when once mixed will never again separate. If light hydrogen or coal-gas be thus placed over a jar of air, the light gas will descend, and render the air explosive. Air is one-third lighter than carbonic acid ; air will support combustion, and it has no effect on lime-water. If a jar of air be placed over one of carbonic acid—in a few minutes the heavy carbonic acid will have risen into the air, a fact proved by lime-water being precipitated white, and a lighted taper being extinguished in the upper jar. This property of gases applies also to vapors, and it leads to a uniformity of mixture on contact, when there is no tendency among them to combine chemically. Such mixtures are of a physical nature, and their properties are always represented by the sum of the properties of their constituents. During mixture, there is no evolution or absorption of heat, and no increase or contraction of volume. The atmosphere itself forms a remarkable example of a mixture of this kind. There are numerous facts in chemistry illustrative of this property. That a gas like ammonia, with a specific gravity of 0·587, should rapidly diffuse itself, and rise through the air is not surprising ; but it may be proved to fall as well as to rise, or, in other words, to diffuse itself in all directions. Place a long (stoppered) shade with its open end in a plate. Suspend from the stopper long strips of dry test-paper for alkalies, *e. g.*, reddened litmus, turmeric, and rose. Now pour on the plate a few drops of a strong solution of ammonia, or open a small jar containing ammonia beneath, the ascent and diffusion of the gas will be indicated by the progressive change of color in the papers as it ascends. By another method of proceeding, the diffusion downwards may be proved. Place a similar shade in a clean plate containing slips of the various test-papers. Remove the stopper of the shade and place over it a small jar containing a few cubic inches of ammonia. In the course of a few minutes the descent (or diffusion) of the light alkaline gas will be indicated by a change of color in the papers. The specific gravity of sulphuretted hydrogen gas is 1·17. A few cubic inches of this will, in spite of its greater density, diffuse itself in the air, and be perceptible in a few minutes in every corner of a large apartment. The same is true of other gases which are not perceptible to smell. The vapor of ether is, perhaps, more remarkable in this respect. Its specific gravity is nearly 2·6. In spite of this great density, the diffusibility of ether vapor is so great, that on opening a bottle containing the liquid, the odor of the escaping vapor will be in a few minutes perceptible over a large space. Even metallic vapors, such as that of sodium, are observed to have this diffusible property. Bunsen found that a small piece of sodium burnt in the corner of a room produced a vapor which was easily detected at the most distant part of the room by the coloring of an invisible jet of gas, and by the spectrum obtained from this light (p. 22). The great natural result of this property, is to equalize mixtures of gases and vapors, and, in open spaces to prevent an accumulation of foul effluvia in the air.

It must not be supposed, however, that specific gravity has no influence on diffusion. On the contrary—the heavy carbonic acid escapes slowly by diffusion from a narrow jar placed with its mouth upwards, while the light hydrogen also escapes slowly from a similar jar placed with its mouth downwards.

A curious fact regarding this property, however, is, that it is manifested not only when the sole communication between the two gases is by a narrow tube, but when they are separated by porous partitions, such as dry plaster, animal membrane, caoutchouc, cork, or spongy platinum. Döbereiner first observed the readiness with which hydrogen escaped through a small crack or fissure in a glass jar which had been filled with the gas. The water rose three inches in a jar from which the gas had thus escaped, clearly proving that the hydrogen had not been replaced by an equal quantity of air passing into the jar. According to Longet, hydrogen will traverse a sheet of writing paper or even gold leaf.

Mr. Graham, on examining Döbereiner's results, observed that while the hydrogen escaped outwards, a portion of air, amounting to between one-fourth and one-fifth of the lost hydrogen, penetrated inwards; in fact, that a volume of air was not replaced by a volume of hydrogen, but by 3·83 volumes. He also found that every gas had what he calls a *diffusion-volume* peculiar to itself, representing the amount in which it was exchanged for a volume of air—air being considered=1 or unity. The diffusion-volume was further found to depend on the sp. gr. of the gas. Of gases lighter than air, the diffusion-volume is greater than 1; of those which are heavier, it is less than 1. The following table represents the diffusion-volume or the velocity of diffusion among different gases:—

Hydrogen	3·83	Oxygen	0·94
Light Carb. Hyd. (CH_2) .	1·34	Sulph. Hyd. (HS) . .	0·95
Carbonic oxide . . .	1·01	Protoxide of Nit. (NO) . .	0·82
Nitrogen	1·01	Carbonic acid . . .	0·81
Olefiant gas	1·02	Sulphurous acid . . .	0.68

An experiment illustrative of the rapid diffusion and endosmosis, as well as exosmosis of gases, may be performed with hydrogen. Fill a wide-mouthed jar with pure hydrogen, and secure the mouth (placed downwards) with a piece of thin sheet caoutchouc. Then place the jar, mouth upwards, under a bell-glass of air immersed in water. The rapid diffusion and exosmose of hydrogen will be indicated by the caoutchouc cover being gradually depressed, and after a time it will burst. This is owing to the place of the hydrogen not being supplied with sufficient rapidity by the passage of air.

If a similar jar is filled with air and placed in a bell-glass of hydrogen, the caoutchouc will rise up in a convex form, showing that the gaseous contents of the jar have greatly increased by the rapid endosmose of hydrogen.

A layer of animal membrane (bladder) may be substituted for caoutchouc with similar results. The fact that gases will thus traverse membranes which would be impervious to them without rupture under direct pressure, has an important bearing on numerous chemical and physiological phenomena. The function of *respiration* is partly dependent on the exchange of gases by diffusion. The oxygen of the air taken into the lungs in all warm-blooded animals, penetrates the fine pulmonary membrane, as well as the thin coats of the capillaries; and it there excludes the carbonic acid of the venous blood. Besides carbonic acid, aqueous vapor containing animal matter is also largely eliminated. Hence the chief phenomena of respiration are due to an endosmose of oxygen and exosmose of carbonic acid, which takes its place. Carbonic acid has been found to escape from blood which was drawn from a vein into a vessel containing hydrogen; thus proving that the blood contains carbonic acid in a free state, and that it is not produced by the combination of oxygen with carbon in the blood circulating through the lungs.

Gases and vapors which admit easily of detection by chemical tests may be proved to traverse membranes with great rapidity. If a wide-mouthed bottle is filled with sulphuretted hydrogen gas, and the mouth is completely closed by a layer of bladder tied tightly over it, it will be found, by the application of paper impregnated with a solution of a salt of lead, that the gas rapidly escapes through the bladder. The paper is turned brown.

If into a similar vessel a small quantity of prussic acid is put, and the mouth is secured by bladder, the rapid escape of the acid vapor will be indicated by inverting on the bladder a watch-glass containing a drop of a solution of nitrate of silver. The solution is whitened in a few minutes, and crystals of the cyanide of silver will be formed in the watch-glass.

The first of the simple gases which will require examination is OXYGEN.

CHAPTER VI.

OXYGEN ($O=8$)—OXIDES—OXIDATION.

History.—Oxygen—one of the six permanent gases, was discovered by Priestley in the year 1774. He obtained it by heating the red oxide of mercury. He called it dephlogisticated air; it was termed empyreal air by Scheele, and vital air by Condorcet. The name oxygen was given to it by Lavoisier, from its tendency to form acid compounds (ὀξὺς, *acid*, and γεννάω, to *generate*). It is more abundantly diffused throughout nature than any of the other elementary bodies; it forms eight-ninths of the weight of water, one-fifth of the weight of the atmosphere, and a large proportion of the mineral bodies of which the crust of the globe is composed. Oxygen is a constituent of a large class of acids—the *oxacids*, which are solid, liquid, and gaseous compounds. It is a constituent of all the alkalies, excepting ammonia, and of the alkaline earths; and it enters largely into the composition of numerous organic substances belonging to the animal and vegetable kingdoms.

Preparation.—This gas may be readily procured by heating in an ordinary retort, by means of a spirit-lamp, a mixture of equal parts of finely powdered peroxide of manganese, previously well dried, and of chlorate of potash. The oxygen is entirely derived from the decomposition of the chlorate, which is converted into chloride of potassium ($KO,ClO_5=KCl+O_6$). The gas may be collected in the usual way over water or mercury. As it is thus procured, it generally contains traces of chlorine, which may be separated by passing the gas, during its collection, through a wash-bottle containing a solution of potash, or by allowing the gas to remain for a short time in contact with water. One hundred grains of the chlorate will yield thirty-eight grains, = about 113 cubic inches of oxygen: or one ounce will yield nearly two gallons of the gas. This is in the proportion of about twenty-eight gallons of gas to one pound of the salt. A mixture in fine powder, of ten parts by weight of chlorate of potash with one part of sesquioxide of iron, has been recommended by Mr. Ashby as superior to the mixture with manganese, in the facility with which oxygen is disengaged, and the great economy of heat. Every grain of this mixture yields a cubic inch of the gas.

Oxygen may also be procured by heating the chlorate of potash separately: but this process requires a much higher temperature, and the employment of a retort or tube which will not readily fuse. This is, however, the only method of procuring the gas absolutely pure for chemical purposes; it should then be collected over a mercurial bath.

Oxygen is obtained on the large scale by gradually heating to full redness in a wrought-iron bottle the black oxide of manganese reduced to a coarse powder. The bottle should be filled to not more than two-thirds of its capacity, and the heat gradually applied. In the first stage of the operation, aqueous vapor and carbonic acid escape; when an ignited match is kindled into a bright flame at the mouth of the tube connected with the bottle, the gas may be collected. The chemical changes which ensue are of a simple kind ($3MnO_2=Mn_3O_4+O_2$). The oxide of manganese, at a full red heat, parts with one-third of its oxygen. Mitscherlich states that three pounds will yield a cubic foot (six gallons) of oxygen; while Dr. Miller assigns five gallons as the quantity obtained from one pound. This difference probably depends on the impurities contained in the native oxide. Among these is carbonate of lime, which contaminates with carbonic acid, the oxygen obtained from manganese. The carbonate may be removed by previously washing the mineral with diluted hydrochloric acid; and if it is subsequently dried before use, oxygen will be obtained from it in a much purer form. Another method consists in mixing the peroxide with sulphuric acid in such proportions as to be of the consistency of cream, and heating the mixture, when oxygen is evolved ($MnO_2+SO_3=MnO,SO_3+O$); but there are some inconveniences attending this process. The bichromate of potash heated with an excess of sulphuric acid also yields this gas ($KO,2CrO_3+5(HO,SO_3)=KO,HO,2SO_3+Cr_2O_3$ $3SO_3+4HO+O_3$), one-half of the oxygen contained in the chromic acid being evolved in this decomposition. Oxygen may be procured from the red oxide of mercury by heating it to redness in a retort ($HgO=O+Hg$). This is an expensive method of procuring the gas, and it is now seldom resorted to; but it has an interest to the chemist from its having been the compound in which this important element was first discovered by Dr. Priestley.

Among recent processes for procuring oxygen, two are deserving of notice. 1. The first depends on the production and decomposition of the peroxide of barium. The peroxide is procured by passing a current of air, deprived of carbonic acid, over baryta heated to low redness in a porcelain tube. If the air is not too dry, oxygen is absorbed by the baryta at a low red heat, and the barium becomes peroxidized. The presence of a small quantity of aqueous vapor in the air is found to be absolutely necessary to this absorption. When the peroxidation is completed, the current of air is cut off, the tube is heated to full redness, and at this high temperature the peroxide is resolved into oxygen and protoxide, or baryta. The oxygen may be collected, and the baryta again peroxidized for a fresh supply. According to Boussingault, a pound of baryta will thus yield about nine gallons of oxygen gas. The baryta itself remains unchanged during the process. This is the only method at present known by which pure oxygen, in the gaseous state, can be readily procured from the atmosphere. 2d. Oxygen has been obtained by causing the vapor of boiling sulphuric acid to pass through a porcelain tube heated to full redness. The retort containing the sulphuric acid is filled with pieces of pumice previously heated with the acid to drive off any chlorides, and the porcelain tube contains the same material. At a full red heat, the products obtained are oxygen, aqueous vapor, and sulphurous acid ($SO_3,HO = O + HO + SO_2$). The sulphurous acid is removed by water or by a solution of carbonate of soda, through which the gaseous products are passed. Two useful salts of soda are thus procured—1, the sulphite employed in the manufacture of hyposulphite; and 2, bisulphite of soda, a salt now much used in chemistry and the arts for the removal of chlorine. This process has been carried out on a large scale by MM. St. Clair-Deville and Debray, and it is stated, with satisfactory results (*Journal de Chimie*, Mai, 1861). M. de Luca, of Pisa, agrees with these chemists in considering that this is the most economical process for obtaining oxygen on a large scale. From a fluid ounce of sulphuric acid M. de Luca states that he procured 360 cubic inches of oxygen. On the large scale, vessels of platinum must be used (*Cosmos*, July, 1861, p. 97).

Properties.—Oxygen gas is insipid, colorless, and inodorous; it is permanently elastic under all known pressures and temperatures. Its specific gravity compared with air, is as 1·1057 to 1·000. Compared with hydrogen, its specific gravity is =16, hydrogen being =1. At mean temperature and pressure, 100 cubic inches weigh 34·24 grains (Dumas and Boussingault). Its refractive power, in regard to light, is less than that of any of the gases; compared in this respect with atmospheric air, it is as 0·830 to 1·000. According to De la Roche and Berard, its specific heat, compared with an equal volume of air, is = 0·9765, and with an equal weight of air, = 0·8848, that of air being =1·000. According to Tyndall, it has, in reference to heat, a lower absorbing and radiating power than other gases. Faraday's researches have shown that it is the most magnetic of all gases, its magnetic force compared with that of the atmosphere being as 17·5 to 3·4, a vacuum being taken as 0, or the boundary between magnetic and diamagnetic gases (*see* page 79). It occupies, among gases, the place which iron holds among metals, and, as with iron, its magnetic force is destroyed by a high temperature; but it returns on cooling. The magnetic properties of the atmosphere are almost exclusively due to the oxygen contained in it, and Faraday has suggested that the diurnal variations of the needle may be referable to the increase or decrease of the magnetic force in the oxygen of the atmosphere as a result of solar heat. Oxygen is evolved by electrolytic action at the positive electrode or anode, and occupies a high position among electro-negative bodies or anïons (*see* page 56).

It is dissolved by water, but only in small proportion. At 60°, 100 cubic inches of water will dissolve 3 cubic inches of the gas, and at 32°, about 4 cubic inches. All terrestrial waters hold it dissolved in much larger proportion than it exists in the atmosphere; and in this condition as a solution of oxygen, it is fitted for the respiration of fish, the blood of these animals, in circulating through the gills, being aërated by the free oxygen dissolved in the water. Oxygen in its pure state is neither acid nor alkaline. It is a perfectly neutral gas; it does not alter the color of blue or red litmus, and shows no tendency to combine with acids or alkalies.

Oxygen eminently supports *combustion*. A lighted wax taper introduced into this gas is rapidly consumed, with enlargement of the flame and the production of an intense light. The wax itself in a melted state, burns in the gas as well as the wick. If a piece of wax taper three or four inches long, be lighted and introduced into a jar of oxygen, with the lighted end downwards, it is speedily consumed, and the melted wax burns brightly as it falls through the gas. A taper (of green wax) with a glowing wick, (of which the flame has been extinguished)—a slip of wood with the end ignited but not burning with flame, or a slip of paper soaked in a solution of nitrate of potash, dried and ignited—will instantly burst into flame when plunged into the gas. If the oxygen is pure, the wax taper or wood may be thus rekindled into flame five or six times successively. A piece of tow saturated with ether and attached to the end of a copper wire, if inflamed and plunged into this gas, burns with surprising intensity, filling the jar with a volume of flame.

In these experiments water (HO) and carbonic acid (CO_2) are the products of combustion, by reason of the oxygen uniting with the hydrogen and carbon of the various combustibles. If a piece of *charcoal* heated to redness be introduced into a vessel of oxygen, it will glow more intensely but be consumed without flame. The whole of the oxygen will be removed and converted into carbonic acid gas, occupying an equal volume but possessed of widely different properties. If a piece of charcoal-bark heated to redness be substituted for charcoal, it will be consumed with bright scintillations traversing the vessel of oxygen in all directions.

Sulphur, which burns in the air with a small blue flame, has the flame enlarged when it is immersed in a jar of oxygen, and after a time it burns with a beautiful purple color, dissolving as it were in the oxygen and converting it into sulphurous acid gas (SO_2), which is soluble in water. If, in this experiment, the bell-glass of oxygen be placed in a white plate containing a diluted solution of blue litmus, the neutrality of oxygen will be indicated in the first instance by the blue color being unchanged; and the production of an acid, by the burning of sulphur, will be demonstrated by the blue liquid being reddened as the sulphurous acid gas is dissolved. The sulphur is not converted to oil of vitrol or sulphuric acid in this experiment. *Phosphorus* burns with a bright yellowish-white light in the atmosphere; but when a piece is kindled by a heated wire and introduced into oxygen, or when kindled in the gas after its introduction, it will burn with a still brighter light, gradually increasing to a dazzling whiteness. If the piece be sufficiently large, the phosphorus after a time will boil, its vapor will be diffused over the whole bell-glass, and burn with equal intensity in every part. The vessel will become an apparently isolated source of the brightest light. The heat is so great, that the vessel is frequently broken in this experiment. The product of combustion in this case is phosphoric acid (PO_5), the highest degree of oxidation of phosphorus. The acid is seen in dense white vapors which readily dissolve in water, and produce a strongly acid liquid; a fact which may be proved by placing a solution of blue litmus in the plate, as in the preceding experiment.

The production of *acids* by the union of oxygen with carbon in any form, with sulphur and phosphorus, led Lavoisier not only to give the name of *oxygen* to this body, but induced him to adopt the hypothesis that the acidity of compounds always depended on the presence of oxygen. But oxygen may produce *alkalies* as well as acids. If a piece of potassium or sodium be heated until it becomes ignited, and is then introduced into the gas, it is consumed with a brilliant combustion, and the product is an alkaline solid, namely, peroxide of potassium (KO_3), in the case of potassium, and sesquioxide of sodium (Na_2O_3) in the case of sodium. If the experiment is performed in a bell-glass standing in a white plate, in which there is a solution of litmus reddened by the product of burning phosphorus, the formation of an alkaline compound, as the result of the combination of oxygen with the metals, will be proved by the blue color of the litmus being restored.

Although the views of Lavoisier respecting the acidifying properties of oxygen have been proved to be incorrect, there is no non-metallic body with which the production of acid properties in compounds appears to be more strongly associated than with oxygen. If a metal combines in various proportions with this element, the first oxide may show no acid properties, but act as a base (*i. e.*, it will combine with acids); but the other oxides are often observed to acquire acid properties in proportion to the amount of oxygen which unites to the metal. This is well illustrated in the oxygen compounds of the metal manganese (*see* page 87). Among the common vegetable acids it is noticed as a general rule, that the number of atoms of oxygen is in excess of those required to produce water with the hydrogen. Among inorganic or mineral compounds, the oxygen acids or *oxacids* are numerous as a class. The hyponitrous, phosphorous, and arsenious acids, as well as the sulphuric, chromic, boracic, and silicic, contain three atoms of oxygen; while the nitric, chloric, bromic, iodic, phosphoric, arsenic, and antimonic acids contain five atoms of oxygen. Some acids contain only two atoms, as the carbonic and sulphurous acids, while others contain only one, as the cyanic. As oxacids for the most part contain an atom of water, and in the absence of water, they manifest no acidity, it has been supposed that the oxygen of the water was really a necessary component of the acid, and that hydrogen was the acidifying principle (*see* page 41). Thus, instead of NO_5HO representing nitric acid, the acid has been regarded as a hydracid, *i. e.*, an acid of hydrogen, represented by the formula HNO_6. According to this view, an acid is convertible into a salt of hydrogen, or a compound of hydrogen with a radical which has not been isolated. But if this be admitted with respect to inorganic acids, it will equally apply to those of the organic kingdom. Thus pyrogallic acid ($C_{12}H_6O_6$) is a solid, anhydrous, crystalline compound, which has no acid reaction, until it is dissolved by water (page 41.) Under these circumstances, it must be assumed, either that the acid now becomes $HC_{12}H_6O_7$, or the hypothesis is unfounded. Although in combining with chlorine, bromine, iodine, sulphur, and cyanogen, hydrogen produces gaseous acids free from water, yet acid compounds exist which not only contain no water, but which are decomposed by that liquid. The fluoboric acid (BF_3) may be taken as an illustration. This body contains neither hydrogen nor oxygen, and is at the same time as much an *acid* gas as hydrocyanic, or any of the hydracid gases above mentioned. But, unlike these, it is resolved by water into two other acids. A similar observation may be made with respect to the fluosilicic acid (SiF_3). The manganic (MnO_3) and fulminic acids (Cy_2O_2) combine with bases to form well-defined salts, but not with water, as no hydrates of these acids are known. The molybdic, tungstic, silicic, titanic, and other acids, can be obtained perfectly anhydrous, and in this state they will expel other acids from bases. The combinations of hydrogen alone prove that there are no sufficient grounds for adopting this hypothesis of the constitution of acids. Hydrogen combines with nitrogen to form a powerful alkaline base, ammonia; but when the three atoms of hydrogen in ammonia, are replaced by three atoms of oxygen, a strong *acid* is the result; and the conversion of the base, ammonia, into nitric acid and water by simple oxidation, is a matter of daily experience. Hydrogen differs from oxygen in forming no *acid* compounds with metals. The only exception is, its compound with tellurium. It is also a remarkable fact, that when the hydrogen is replaced by oxygen in some organic compounds, an acid frequently results. In the acetous fermentation, the conversion of alcohol to vinegar or acetic acid is the result of simple oxidation. One-half of the hydrogen is removed—the proportion of oxygen is increased, and as a result of these changes, the neutral compound, alcohol, is converted into acetic acid. Another remarkable instance of the acidifying effect of oxidation is furnished by the pure essential oil of bitter almonds. This liquid, dissolved in alcohol, is perfectly neutral. As the alcohol evaporates, the oil is oxidized, and is converted into solid crystallized benzoic acid. The only chemical change here is the substitution of oxygen for hydrogen; and as this goes on, the neutral is observed to be converted into an acid compound. Hydrogen has therefore no claim to be regarded as an acidifying principle in preference to oxygen. The name given to this element by Lavoisier is fully justified by modern researches, with the qualification that it is not the only acidifying element. In fact, acidity, like alkalinity, is a condition or property resulting from the chemical union of bodies; and is not essentially dependent on the presence of any one substance. There appears to be no good reason, therefore, for converting the oxygen-acids to hydracids by the supposed decomposition of the water associated with them.

Oxygen not only produces, as a result of chemical union, acids and alkalies, but it forms with the greater number of metals, binary compounds which are quite *neutral;* and in order to distinguish these from other products, they are called *oxides.* With some of the metals, when heated to a high temperature, the phenomena of combustion are splendidly manifested. Thus *zinc* in foil or shavings, may be formed into a bundle two or three inches long (the ends being tipped with a little melted sulphur, for the purpose of igniting the metal); on introducing the ignited zinc into a tall bell-glass of oxygen, there is a brilliant combustion of the metal. The light evolved is of an intense greenish white color, and a white flocculent product results, which is oxide of zinc (ZnO). The finest *iron-wire* made into a bundle, tipped with sulphur, ignited, and introduced into a large vessel of the gas in a pure state, burns with an intense white light, and with scintillations of fused metal, which sometimes penetrate the substance of the glass. Rounded masses of the fused iron, oxidized, fall at a white heat (3280°), with hissing noise, into the water of the vessel in which the gas is placed. The compound produced in this experiment is the magnetic oxide of iron (F_3O_4, or $FeO + Fe_2O_3$). The heat being sufficient to drive off a portion of the oxygen, which in the first instance produces a peroxide of the metal.

Oxidation.—Oxygen combines with some bodies directly, and at all temperatures. A jar containing deutoxide of nitrogen (NO_2), when exposed to oxygen gas, or to any mixture containing free oxygen, forms deep ruddy vapors of an acid nature. The neutral deutoxide is further oxidized, and is converted to an acid of nitrogen. If iron filings, moistened with water, are thrown into a jar of oxygen gas, and the particles of metal are diffused by agitation, so as to adhere to the inner surface of the glass, and the jar is inverted in a vessel of water, the oxygen is slowly but completely removed without the evolution of light and heat, while the water rises in the vessel. The iron takes the oxygen and is converted to peroxide. If this experiment is performed in a jar containing air, the water rises to about one-fifth of the capacity of the vessel, thus indicating not only the presence of oxygen, but the proportion of that element in air. With some substances oxygen will combine, but only indirectly, or by the aid of complex chemical affinity. As examples of this kind may be mentioned chlorine, bromine, and iodine. Oxygen as a gas has no tendency to unite with these elements. With fluorine it forms no known combination. In order to combine with oxygen in a free state most substances require to be heated above the ordinary temperature of the atmosphere. Thus phosphorus has no tendency to form a compound with pure oxygen below a temperature of 80°; but when oxygen is mixed with nitrogen (as in the atmosphere), or with other gases, phosphorus will enter into combination with it at 32°, and even at temperatures below this. The phosphorus is slowly oxidized, being converted into a deliquescent liquid—phosphorous acid (PO_3); and, during the combustion, the phosphorus appears luminous in the dark. Phosphorus does not commonly enter into combustion in oxygen below its melting point (112°), while, in the allotropic state, it may be heated to nearly 500° without taking fire. Free oxygen, as it exists in the atmosphere, appears to have no tendency to combine with carbon below a red heat (1000°)—with hydrogen below 600°—with zinc below its vaporizing point (1900°)—or with sulphur below 500°. This want of action at low temperatures appears to depend less on the absence of affinity between oxygen and the substance, than on the effect of cohesion on the substance exposed to the gas. When phosphorus, iron, and even lead, are reduced to a fine state of division, and exposed to oxygen at any temperature, they will take fire, and burn with the same brilliancy as larger masses which have been heated. (See PYROPHORI, page 40, also COMBUSTION.)

In the process of *oxidation* oxygen may form a gaseous, liquid, or solid compound, either quiescently or with the phenomena of combustion. A simple substance may enter into combination with oxygen in various proportions, and it is then found that while the compounds which contain the smallest proportions of oxygen are neutral oxides, those which contain the largest proportions have acid properties, and unite with bases to form salts. The metal manganese (Mn) affords a remarkable instance of this series of combinations. Thus we have MnO, or *Protoxide* of manganese, which combines with acids to form the salts of this metal—MnO_2 *Binoxide* or *Deutoxide*—names which indicate the number of atoms of oxygen, combined with the metal. *Peroxide* (hyperoxide from υπὲρ, higher) is a term applied to an oxide beyond, or a higher stage of oxidation; this, without reference to the number of atoms, indicates the maximum degree of oxidation. Thus while the peroxide of copper has one atom of oxygen (CuO), and that of iron one and a half atoms (or three to two of metal), the peroxide of lead has two atoms (PbO_2) and that of nitrogen four atoms (NO_4). The metal manganese furnishes compounds in other stages of oxidation; thus there is a sesquioxide, Mn_2O_3, signifying that the oxygen is $1\frac{1}{2}$ to 1 of the metal, or, to avoid the use of fractions, 3 to 2. There is next in order a compound of the sesquioxide with the protoxide, called, from its color, the red oxide of manganese, represented by the formula (MnO,Mn_2O_3), or Mn_3O_4. Beyond this there are two acid compounds, manganic acid MnO_3, and permanganic acid Mn_2O_7. The compounds of oxygen and manganese, which represent all the varieties, and at the same time the greatest range of combinations of oxygen in mineral chemistry, stand as follows:—

Name.	Formulæ.	Atoms O.		Wt. Ox.	At. Mn.		Wt. Mn.
Protoxide . . .	$Mn\ O$	1	=	8	1	=	28
Deutoxide . . .	$Mn\ O_2$	2	=	16	1	=	28
Sesquioxide . . .	Mn_2O_3	3	=	24	2	=	56
Red oxide . . .	Mn_3O_4	4	=	32	3	=	84
Manganic acid . .	$Mn\ O_3$	3	=	24	1	=	28
Permanganic acid . .	Mn_2O_7	7	=	56	2	=	56

There are degrees of oxidation in which the metal is in larger proportion than the oxygen. These are called *suboxides*. Thus the suboxide of copper is represented by the formula Cu_2O; it is a compound of one atom of oxygen with two atoms of metal.

The tendency of the oxides of metals to combine with acids to form salts is materially influenced by the stage of oxidation. The protoxide is the compound which usually possesses strong basic properties, and which, by combining with acids, produces the large variety of metallic salts. Chemists generally fix upon the protoxide by this combining character. If a suboxide is acted upon by an acid, one atom of the metal is set free, a protoxide results, and this forms a salt. Thus, in boiling suboxide of copper with diluted sulphuric acid, metallic copper is deposited, and a sulphate of the oxide of copper results ($Cu_2O = Cu + CuO$). On the other hand, when a peroxide is treated with an acid, an atom of oxygen is given off. Thus when peroxide of barium is treated with sulphuric acid, sulphate of the protoxide of barium is produced, while oxygen escapes as a gas ($BaO_2 = BaO + O$). On this principle, as it has been already explained, peroxide of manganese may be made to yield oxygen by heating it with sulphuric acid. (*See* page 82). Sesquioxides may combine with acids to form salts; this is seen in the sesquioxides of iron, aluminum, and chromium; and as the protoxide, containing one atom of oxygen, requires one atom of acid for producing a neutral salt, so the sesquioxide, containing three atoms of oxygen, requires three atoms of acid to form the class of sesquisalts. The oxides which have the peculiar constitution of three atoms of metal to four of oxygen, may be regarded as compounds of two other oxides, and are resolvable into these by acids. In consequence of this union or mixture, they have been sometimes called saline oxides—the one oxide being supposed to act as a base to the other. Examples of these oxygen-compounds occur not only in manganese, as above stated, but in iron and lead. The magnetic oxide of iron—the mineral which alone permanently retains magnetic force—is an oxide of this description. It is represented by the formula Fe_3O_4, which is convertible into oxide (FeO) and sesquioxide (Fe_2O_3) of iron. The substance called red lead is a compound oxide, having the formula Pb_3O_4, but resolvable by acids into $2PbO$ and PbO_2. When this oxide is digested in nitric acid, the acid forms with the protoxide nitrate of protoxide of lead, soluble in water, while the peroxide is left unacted on as a heavy, dark-brown insoluble powder.

Some metals appear to have no stages of oxidation, in which basic or neutral compounds are produced. In the lowest degrees of combination with oxygen they at once form acids. Arsenic furnishes an example of this kind: this metal combines with three atoms of oxygen to form arsenious acid, (AsO_3) and with five atoms of oxygen to form arsenic acid (AsO_5). Antimony, which presents so many analogies to arsenic, forms a teroxide with three atoms of oxygen (SbO_3), and an acid with five atoms, antimonic acid, (SbO_5). These combine to form a compound which has the remarkable composition of Sb_2O_8, and is called antimonious acid.

Reduction.—While the term *oxidation* implies simply the combination of oxygen with bodies, the term *reduction* implies the separation of oxygen from substances by chemical agency, and the conversion of them into their original state of metal or combustible. The term *regulus* was formerly applied to the metal thus derived from an oxide, and the reguline state, therefore, simply implies the non-oxidized state. The word reduction, however, is equally applied by modern usage to the separation of the metals from chlorides, sulphides, and similar binary compounds.

Respiration and Combustion.—Oxygen is the great supporter of respiration and combustion, and is largely consumed in these processes; hence air deprived of oxygen by either process, or by ordinary chemical changes, is unfit to support animal life, and will not allow of the combustion of other bodies. If a lighted wax taper be introduced into a jar of air, in which iron filings have been sprinkled with a little water, it will be found, after some hours, that the residuary gas will extinguish it; and any small animal introduced into this residuary gas, would be instantly rendered lifeless. 1. If we breathe by a wide tube into a bell-glass filled with water, and inverted on a water-bath, so that the water may be displaced by the expired air as it issues from the lungs—we shall find on introducing a lighted wax-taper that it will be instantly extinguished. 2. A lighted taper introduced into a bell-glass of air, placed over a water-bath (the bell-glass being closed at the top by a brass-plate or stopper), will be extinguished in a few minutes, owing to the rapid consumption of oxygen and the absence of any fresh supply. On removing the extinguished taper quickly and introducing another, lighted, this will also be extinguished; and any small animal placed in either of these mixtures, thus deprived of a large portion of their oxygen, would soon perish. It must not be supposed, however, that *all* the oxygen is removed from air, either by respiration or by ordinary combustion. That there is still some portion left in the vessels, may be proved by introducing into them a ladle containing a small piece of phosphorus ignited. This will continue to burn at the expense of the residuary oxygen not removed by the lungs in breathing, or by the wax-taper in combustion. Air, therefore, which is deoxidized, or which does not contain a certain amount of free oxygen, is wholly unfitted to support life. Respiration and combustion vitiate it by withdrawing oxygen and supplying its place with carbonic acid. As a general rule, an animal cannot live in air in which a wax-taper will not burn, and a taper will not burn in an atmosphere, in which there is too small an amount of oxygen to maintain respiration.

If our atmosphere had consisted of oxygen alone, combustion once set up would not have ceased until all combustible substances had been consumed, and the whole face of the earth changed. So in regard to animal life, although oxygen is absolutely necessary to respiration—when this gas is in a pure state, *i. e.*, unmixed with nitrogen—it operates as a powerful excitant to the nervous system; and a small animal confined in an atmosphere of pure oxygen will die in a few hours, apparently from the excessive stimulus produced by the gas. Mr. Broughton determined, experimentally, that rabbits died in six, ten, or twelve hours when confined in oxygen. On examination after death, the blood was found highly florid in every part of the body; and the heart continued to act strongly even after respiration had ceased. The dilution of the oxygen of the atmosphere with four times its volume of nitrogen is therefore absolutely necessary to animal life. It is worthy of notice, however, in reference to this noxious action of pure oxygen, that an animal will live three times as long in this gas as when it is confined in an equal volume of common air. The reason for the difference is, that the quantity of oxygen in air available for respiration is not only four-fifths less, but that which has been consumed by the animal is replaced by an equal bulk of carbonic acid, which is itself a noxious gas.

Decay.—Eremacausis.—Putrefaction.—Oxygen takes an important share in these processes. It is by slow oxidation that organic are converted into inorganic compounds; and these again, by means of the vegetable kingdom, are reconverted into organic substances fitted for the food of animals. In the slow oxidation of vegetable matter, we have an example of that condition, which has been called by Liebig *eremacausis* (ἠοέμα slow, καῦσις burning). If fine sawdust, moistened with water, is placed in a stoppered bottle containing air, and exposed for some time to a temperature above 60°, it will be found that the oxygen of the air in the bottle has been to a greater or less extent replaced by carbonic acid. A lighted taper, introduced into the bottle, will be extinguished, and carbonic acid may be proved to be present by the usual tests. Under these circumstances, there is no sensible heat or light evolved; hence the term combustion, applied to this kind of oxidation, is not strictly correct. In certain cases, however, the accumulation of heat as a result of the oxidation of some kinds of vegetable matter is such, that the mass, if easily combustible, may burst into flame. Cotton, flax, tow, jute, and other vegetable substances of a porous nature in a damp or greasy state, are thus subject to spontaneous combustion, as a result of slow oxidation. Thin gutta percha appears to undergo both physical and chemical changes from the absorption of oxygen. It becomes altered in color and tenacity by long exposure to the air; and although it does not inflame, it may, when exposed in large surfaces to air, acquire a temperature sufficient to melt it. This is probably the real cause of the heating of electric cables in the holds of vessels in which they have been stored. All cases of oxidation are attended with the evolution of heat, but when the process is slow, the evolved heat is unobserved and dissipated without accumulation; in other cases, when the process is effected in a shorter period, the heat becomes proportionably sensible; and when the oxidation is rapid, the whole of the heat being evolved in a much more limited time, it is proportionably exalted in intensity.

Oxygen takes an important share in the acetous *fermentation*, as it is by the oxidation of the elements of alcohol that acetic acid is produced. In some of its combinations it exerts a *deodorizing* or disinfecting power. Thus, as it is set free from a solution of permanganate of potash or soda, it oxidizes and destroys all the offensive products evolved in the decomposition of organic matter, which generally consist of compounds of hydrogen, with sulphur, nitrogen, phosphorus, and carbon.

Equivalent.—The equivalent or combining weight of oxygen is generally taken as 8, compared with hydrogen as unity; and in reference to its volume-equivalent in its combinations with other gases, it is one-half of that of hydrogen, or one-half volume.

Tests.—*Special Characters.*—Oxygen may be known as a gas in the free state: 1. By its insolubility in water, or in a strong solution of potash. 2. By its entire solubility in potash to which pyrogallic acid has been added. 3. By its kindling into flame, an ignited match or the glowing wick of a taper. There is only one other gas known which possesses this property, namely, the protoxide of nitrogen (NO); but there are other well-marked distinctions between this gas and oxygen. 4. Oxygen produces red acid fumes when deutoxide of nitrogen (NO_2) is added to it. 5. It changes the white ferrocyanide of iron to Prussian blue.

When oxygen exists in the uncombined state, but dissolved by liquids, such as water, its presence may be readily detected by the white proto-ferrocyanide of iron. This test-liquid should be made for the occasion. It may be prepared by shaking in a small bottle a mixture of bright iron filings and a fresh solution of sulphurous acid gas. After a few minutes the liquid should be filtered and diluted with water; a small quantity of a solution of ferrocyanide of potassium should then be added to it. A milky-white precipitate of the proto-ferrocyanide is thrown down. This rapidly becomes blue on the surface by absorbing oxygen, and passing to the state of sesqui-ferrocyanide of iron, or one variety of Prussian blue. If this liquid be poured into a jar of oxygen gas, and the jar shaken, it will speedily be converted to Prussian blue. If poured in a thin sheet on a white plate, it will reveal the presence of oxygen in the atmosphere, by its rapid change of color on the surface. If we add a little of the test-liquid gradually to eighty or one hundred ounces of water containing free oxygen, in a tall glass jar, it will be observed that, as it falls through the water, it will change from white to blue, by absorbing and fixing the dissolved oxygen.

The whole of the free oxygen may be removed from a gaseous mixture, by dissolving pyrogallic acid in a strong solution of potash, and introducing the mixture into a vessel containing the gas over mercury. If the vessel is graduated, the proportion of oxygen present may be thus determined. If carbonic acid, or any other acid gas should be present, these may be removed by first passing a solution of potash only into the tube, and when no further absorption takes place, the level may be taken, and pyrogallic acid added to the potash. The further absorption will then indicate the amount of oxygen. The quantity of free oxygen may be more accurately determined, by adding to the gaseous mixture its volume of pure hydrogen, and then bringing about its combination with oxygen, either by the electric spark or by the aid of spongy platinum. This process will be more fully explained in treating of the composition of water. Oxygen may also be removed from a mixture of gases, by causing it to pass over metallic copper heated to redness in a tube.

CHAPTER VII.

OXYGEN—INCANDESCENCE—COMBUSTION—DEFLAGRATION.

Combustion with and without Oxygen.—Combustion, in its most extensive meaning, may be described as the result of intense chemical combination between two or more bodies, during which sensible light and heat are evolved. All ordinary cases of combustion are dependent on the combination of *oxygen* with bodies; and the heat and light are dependent on the rapidity with which oxidation takes place, as well as on the amount of oxygen consumed. Lavoisier believed that oxygen was the universal supporter of combustion, and that there was no combustion without it. In this, however, he was in error. The phenomena of combustion are seen in some of the combinations of chlorine, bromine, and sulphur with bodies. If phosphorus is introduced into a jar of chlorine, it speedily melts, takes fire, and burns with a pale yellowish flame, forming chloride of phosphorus. If thin leaves of Dutch metal are introduced into chlorine, they burn without flame, producing a full red heat, and forming chloride of copper. Freshly powdered metallic antimony projected into chlorine gas, burns in scintillations, evolving much light and heat, and forming white chloride of antimony: if this metal in fine powder be projected into bromine, it burns, in contact with the liquid, with bright scintillations, forming bromide of antimony. So with regard to sulphur; if this substance is heated in a Florence flask to its vaporizing point, it forms a dark amber-colored vapor, in which thin pieces of copper foil, or cuttings of copper, glow and burn with great splendor, producing sulphide of copper. The metal sodium heated in air until it begins to take fire, when plunged into a jar of chlorine, will burn with the most intense evolution of light and heat, and sometimes with explosive violence. The ladle holding the metal acquires a red heat as a result of this combustion. Fine steel wire previously heated to redness also burns with a deep lurid glow in chlorine. These experiments will clearly show that oxygen is not in all cases necessary to combustion; and that the phenomena which attend it, cannot be regarded as dependent upon any peculiar principle or form of matter; they must be considered as a general result of intense chemical union. Each substance, in fact, has its own special properties in reference to combustion. Sulphur will not burn in chlorine; and to cause it to burn in oxygen, it must be heated to a high temperature. Copper will not burn in oxygen gas, but it will burn at the lowest temperature in chlorine. Phosphorus will not undergo combustion in oxygen below a temperature of 80°; but it will take fire in chlorine at 32°.

Some compound gases may give rise to the phenomena of combustion with alkaline metals under certain conditions. Cyanogen gas is a compound of carbon and nitrogen. If potassium is heated in a current of this gas, the metal burns, and leaves as a product cyanide of potassium. Again, if sodium be heated in a flask from which air is entirely excluded, and a current of dry carbonic acid is passed through the flask, a brilliant combustion will take place, the oxygen of the carbonic acid being taken by the sodium to form soda, while carbon is deposited. Cyanogen and carbonic acid are not usually regarded as bodies which support combustion, and the latter is commonly regarded as incombustible.

Confining our views for the present to combustion as it takes place in *oxygen*, it may be remarked that there is no loss of matter but merely a change of state. If a spirit-lamp is accurately balanced in a scale-pan, and the wick then ignited—as the spirit burns, there will be an apparent loss of matter, and the counterpoised scale will sink. If we hold over the burning wick, the open mouth of a gas-jar, we may be able to prove by appropriate tests, that the air of the jar is replaced by carbonic acid and aqueous vapor—the latter being condensed on the inner cold surface of the glass. These products are formed at a high temperature by the oxidation of the carbon and hydrogen contained in the vapor of alcohol. If collected in a proper apparatus, the weight of these products would be equal to the weight of alcohol consumed.

If a piece of phosphorus is heated in a vessel of pure oxygen, all the oxygen disappears, but it is now solidified as phosphoric acid, and the increase in the weight of the phosphorus would represent exactly the amount of oxygen consumed. In the burning of carbon there appears to be no loss of gaseous matter; but the oxygen in this case is converted into carbonic acid; and it will be found, although unaltered in volume, to have acquired an increase in weight equal to the weight of carbon consumed. Substances which undergo combustion in oxygen are rendered heavier; the weight of oxygen taken during combustion, is always added to the original weight.

When a metal burns in oxygen, it is oxidized with the evolution of light and heat; but a metal may be oxidized without undergoing combustion in the ordinary sense. Zinc and lead furnish striking instances of the difference. If zinc be heated in air to above its melting point, it will take fire and burn with a splendid greenish-white light (*see* page 86); but if lead be melted in air, there is formed on the surface a dirty yellowish-looking film or dross (oxide of lead), without the evolution of light and heat. Both are instances of oxidation, but in the latter case there is no combustion.

Ignition.—Incandescence.—Combustion always implies chemical action: either the heat of the combining bodies or that which results from their combination is set free, and with this, a proportionate quantity of light; but a body may evolve heat and light without undergoing combustion or any chemical change. Thus a platinum wire, some fibres of asbestos, or a piece of lime, exposed to the strong heat of an invisible flame—*e. g.*, of oxygen and hydrogen—may be heated to whiteness, so as to evolve both heat and light of surprising intensity. To this state the term *ignition*, or incandescence, is applied. The body evolves light as a result of its being intensely heated, without its molecules being materially altered in their physical or chemical relations. It is not fused at the temperature to which it is exposed; and the greater the amount of heat which it is capable of receiving without a change of its physical condition, the more intense the light which is emitted. An ignited body, therefore, serves as a temporary storehouse of heat and light. The vacuum-light furnishes a remarkable instance of the results of ignition. The charcoal points, being the terminal poles of a powerful battery, are inclosed in a glass vessel in which a vacuum has been artificially produced. The light issues in great splendor as the result of the ignition of minute particles of charcoal carried between the poles, but the charcoal itself undergoes no combustion. When platinum poles are used, portions of that metal are volatilized and so heated as to give out the intense violet-blue light which characterizes the spark. Mr. Gassiot has observed, that under these circumstances the negative pole assumes the appearance of being corroded, owing, as he found, to the separation of particles of this metal and their deposition on the sides of the vacuum-glass tube. Even *gases* attenuated to the highest degree—in fact, almost converted into a vacuum by the air-pump—may be rendered incandescent by the discharge of the spark from Ruhmkorff's coil (*see* page 77). In an absolute vacuum no discharge passes, as electrical conduction necessarily requires the presence of matter; but Mr. Gassiot's experiments have proved that what has been hitherto regarded as a vacuum, is space filled with highly attenuated matter, capable of being made incandescent by the electric discharge. The more attenuated the gas or vapor, the more stratified is the light of the discharge. As the gas is increased in quantity, the stratifications become closer, until at a certain point, the discharge entirely loses its stratified appearance and passes into a wave line. The vivid luminosity and the varied color of lightning, is probably dependent on the incandescence of the gaseous and vaporous constituents of the atmosphere, modified by the density of the stratum in which the electric discharge takes place.

The color of the light of incandescence is not always the same for the same gas. Thus while Dr. Miller found that a hydrogen vacuum gave a red, and a nitrogen vacuum gave a violet light (*see* page 77), Mr. Gassiot observed in his experiments, that hydrogen gave a greenish-white, and nitrogen a red light. We are informed by Mr. Gassiot, that oxygen in an incandescent state resembled hydrogen in color, but the light was less green; and sulphurous acid, rendered incandescent, had an intense blue color. The color may probably be affected by the degree of rarefaction of the gas, the temperature, the presence of aqueous vapor, and other circumstances.

In the attempt to render compound gases and vapors incandescent, some remarkable effects have been observed. Thus Plücker found that when seleniuretted hydrogen was exposed to the current, selenium was deposited on the sides of the glass vessel, and the spectrum of hydrogen appeared. After a short interval, the two elements again combined, and the spectrum peculiar to seleniuretted hydrogen replaced that of pure hydrogen.

It is found that the greater number of *metals* may be converted into vapor, and that these vapors when rendered incandescent by the current, emit a light varying in color for each metal. For the purpose of obtaining the metals in a volatile state, the platinum poles are moistened with the respective solutions. M. Faye found that zinc gave a blue color in strata or bands; antimony, a lilac color; mercury, a pale blue; cadmium, an intense green; arsenic, a magnificent lilac; and bismuth, a variety of colors, undergoing rapid changes. (*Cosmos*, Sept. 20, 1861, p. 321.) It has been further proved that these colored flames and incandescent vapors present colored spectra of differently refrangible rays, in some instances characteristic of the substance. (*See* page 59.)

Supporters and Combustibles.—Although oxygen, chlorine, and bromine give rise to the phenomena of combustion with other bodies, they cannot be made to combine with each other, so as to evolve light and heat; and hence they are said to be incombustible. In ordinary language they are called *supporters* of *combustion*, while the bodies to which they unite have been called *combustibles.* It is, however, generally admitted that the phenomena of combustion are dependent on the union of the two bodies; and that the so-called supporter is consumed as well as the combustible, and aids in furnishing light and heat. Thus copper and sulphur, at a high temperature, combine with combustion. Which is the supporter and which the combustible? Both must be regarded as combustible substances—for copper burns in chlorine, and sulphur burns in oxygen. Whether we put phosphorus into the vapor of chlorine, or chlorine into the vapor of phosphorus, the same kind of combustion equally ensues, and the products are similar. During the combustion of phosphorus in oxygen the intense and sudden burst of light which appears after the phosphorus has entered into the boiling state, arises from the diffusion of its vapor throughout the oxygen of the vessel, so that there is a combustion of both at every point of contact. Up to this time the light and heat may have appeared to proceed from the solid phosphorus only; but it will now be observed to issue equally from all parts of the vessel containing the oxygen. The oxygen is here as much a combustible as the phosphorus. In fact, the term "combustible" is relative and arbitrary; that body which is for the time in larger quantity, or in the gaseous state, is called the "supporter." Coal-gas burns in oxygen or air only where it can unite with oxygen; and it is therefore called a combustible gas. If we kindle a jet of coal-gas issuing from a bladder, and cause the flame to be projected into a bell-glass of oxygen, it will burn brilliantly. If we fill another bell-glass with coal-gas, ignite it at the mouth, and project into it through the flame a jet of oxygen, this gas will appear to burn, and in fact does burn, in a jet precisely like the jet of coal-gas; and it will be found to give out the same amount of light and heat, and to give rise to similar products. The oxygen and coal-gas burn only where they meet each other at a high temperature. The oxygen burns in an atmosphere of coal-gas just as certainly as the coal-gas burns in an atmosphere of oxygen. This experiment may be performed with an ordinary argand gas-burner. A long chimney-glass should be placed over the burner, and all access of air from below cut off by a cork and a disk of card. If, after allowing the coal-gas to issue for a few minutes, in order to remove the air, it is ignited at the top of the chimney-glass, a jet of oxygen may be safely propelled downwards through the gas-flame, and the oxygen will appear to burn in the glass cylinder containing the coal-gas. These facts show that combustion is really a reciprocal phenomenon, each body burning, or, in chemical language, combining with the other body, and, during this combination, evolving light and heat. The terms combustible and supporter of combustion are, however, convenient for use, provided we understand by them that each substance shares in the process, and that neither is, strictly speaking, passive.

Heat and Light of Combustion.—The results of experiments on some substances show that the *heat* of combustion is almost exclusively derived from the oxygen. Thus it appears, from the researches of Despretz, that the *heat* depends, not upon the quantity of combustible, but upon the weight of oxygen, consumed. A pound of oxygen, in combining respectively with hydrogen, charcoal, alcohol, and ether, evolved in each case very nearly the same quantity of heat, each raising 29 pounds of water from 32° to 212°. With respect to the comparative heating powers of equal weights of different combustibles, he obtained the following results :—

1 pound of	hydrogen raised	236	pounds of water	from 32°	to 212°
"	oil, wax	90	"	"	"
"	ether	80	"	"	"
"	pure charcoal	78	"	"	"
"	common wood charcoal	75	"	"	"
"	alcohol	68	"	"	"
"	bituminous coal	60	"	"	"
"	baked wood	36	"	"	"
"	wood holding 20 per cent. of water	27	"	"	"
"	turf (peat)	30	"	"	"

This table indicates, not the absolute amount of heat evolved, but the relative heating powers of fuels burnt under similar conditions; and it further appears to show that, provided the same weight of oxygen be consumed, whatever may be the nature of the fuel, the same amount of heat will be evolved. In order to produce an intense heat therefore, the object is not so much to consume the fuel as to consume the maximum of oxygen with a minimum of fuel. The heating power of the blowpipe and of the blast-furnace, especially of the *hot* blast (to counteract the cooling effect of the nitrogen associated with oxygen in the air), will now be intelligible on chemical principles. It is not, however, strictly true that the same weight of oxygen always produces by combination the same amount of heat. Other experiments performed by Despretz have shown that a pound of oxygen, in combining with iron, tin, and zinc, could heat nearly twice as much water to the same temperature as that which in his table he assigns to hydrogen, carbon, alcohol, and ether; hence, in reference to these metals, oxygen alone cannot be concerned in its production. So with regard to phosphorus: if this substance is burnt slowly, to produce phosphorous acid, a pound of oxygen in combining with it evolves the same amount of heat as that assigned to carbon and hydrogen; but if the combustion is so intense as to produce phosphoric acid, then the heat evolved is twice as great, resembling that which is given out in the intense combustion of iron, tin, and zinc. There is another fact which shows that the rule regarding the evolution of heat is not so simple as Despretz had supposed; namely, that when carbon is in a state of combination, as in the form of carbonic oxide, the amount of heat evolved during its combustion and conversion into carbonic acid, is nearly equal to that which would be evolved by the carbon in a separate state, although the latter would require twice the amount of oxygen to convert it to the same product (carbonic acid). (*Kane's Elements of Chemistry*, p. 244). The later researches of Professor Andrews and other chemists have shown, that the quantity of heat evolved as a result of the chemical combination of bodies is definite, and that it has a specific relation to the combining number of each substance. With a proper supply of oxygen, or air, a given weight of the substance always produces the same amount of heat.

Hydrogen, carbon, sulphur, and phosphorus are the four principal substances, with which the phenomena of combustion are witnessed in an atmosphere containing oxygen. All our ordinary sources of light and heat for domestic and manufacturing purposes are dependent on the two first-mentioned elements, associated in variable proportions in coal, wood, and oil. The following table will show that according to the experiments of Despretz, hydrogen and carbon, weight for weight, consume the largest amount of oxygen in undergoing perfect combustion; and that hydrogen in uniting to oxygen has more than three times the heating power of carbon :—

	Pounds of Oxygen.		Pounds of Air.	Prop. of Comb. to Oxygen.
1 pound of hydrogen takes	8	or	40	1:8
6 pounds of carbon take	16	or	80	1:2·6
16 pounds of sulphur take	16	or	80	1:1
32 pounds of phosphorus take	40	or	200	1:1·25

Hence by reason of this enormous consumption of oxygen in proportion to the weight of material burned, hydrogen, and bodies containing it, evolve the greatest amount of heat. Hence also in the oxy-hydrogen blowpipe, we have one of the highest sources of heat at present known; and as an indirect result of the absorption of this heat by the infusible substance, lime, we obtain a light which rivals that of the sun in intensity and chemical power. Lately, by the construction of a close furnace of lime, and the use of the oxy-hydrogen blowpipe, MM. Deville and Debray have not only been able to volatilize many of the supposed fixed impurities in commercial platinum; but with about 43 cubic feet of oxygen they have succeeded in melting 25 pounds of platinum in less than three quarters of an hour, and casting it into an ingot in a coke mould. All metals are melted, and many are entirely dissipated in vapor by the intense heat produced under these circumstances. The lime itself is unaltered by the heat, and acts as a powerful non-conductor, even when not more than an inch in thickness. Lime and magnesia appear hitherto to have resisted fusion, or volatilization as oxides. The heat given out during the perfect combustion of hydrogen in oxygen was calculated by Sir R. Kane (*Elements of Chemistry*, p. 240) to amount to 5478° above the freezing point; but this estimate falls far below that assigned by the recent experiments of Bunsen. (*See* p. 98.) This temperature exceeds the heat of other artificial sources. It can only be surpassed by the heat of the electric discharge, or by the concentration of the rays of the sun through a powerful lens or mirror. When hydrogen is burnt in atmospheric air, the cooling effect of the nitrogen is such that, according to the same authority, the heat does not exceed 2739° above freezing; this is nearly equal to the melting point of cast iron, which is 2786°.

According to Pouillet, the temperatures for the different degrees of heat of solids in a state of ignition, referred to in chemical works are as follows:—

Dull red heat	700°	Yellow red	1100°
Cherry red, commencing	800°	Bright ignition	1200°
Brighter	900°	White heat	1400°–3280°
Full red heat	1000°		

In reference to combustion, the improvements made in the use of gas as a source of heat have depended on the admixture of air or on the free supply of air by a variety of arrangements; and in the construction of all furnaces, the adoption of this principle leads to an economy of fuel, the prevention of smoke, and the production of the largest amount of heat.

The *light* evolved in combustion depends—1. on the intensity of the heat; and, 2, on the presence of solid non-volatile matter which is capable of receiving the heat, and of emitting it as light. When combustion takes place at a low red heat, as in the aphlogistic lamp of Sir H. Davy, there is but little light. In fact, this is only visible in the dark. Hydrogen burns with intense heat; but as watery vapor is the only product, there is no solid matter to absorb and emit the heat as light. If platinum wire, or particles of charcoal, lime, asbestos, or iron-filings are introduced into the flame, they are heated and emit light. The bright white light emitted by coal-gas is owing to the particles of carbon, set free during the combustion of the gas, acquiring a white heat, and becoming incandescent in the flame. The naphthalizing of ordinary coal-gas depends on the diffusion through it of a hydrocarbon vapor, which, during combustion, may furnish particles of carbon to the flame. In burning phosphorus in chlorine, a gaseous chloride is produced, and the phosphorus burns with a pale flame, emitting but little light; but when it is burnt in oxygen it forms dense solid particles of phosphoric acid, which being strongly heated emit an intensely white light. The difference of light arising from the products may be shown by raising the phosphorus, which has been burning in a bell-jar of chlorine, into the atmosphere. The increased splendor of the combustion from the formation of a solid product is at once manifested, and the effect is increased by plunging the ladle with the burning phosphorus, into a bell-jar of oxygen. In burning zinc the same phenomenon is observed;—the oxide of zinc produced is a solid body, which becomes intensely heated and emits a large amount of light. If a piece of magnesium wire be ignited in a Bunsen's jet, a most dazzling white light is evolved, arising from the fixed particles of the oxide of magnesium becoming strongly heated, and, as a result of this, evolving a light of the greatest intensity. In some photo-chemical investigations made by Bunsen and Roscoe, it was calculated that the light of the sun's disk was only 524 times as great as the magnesium light. A wire of about the 1-100th of an inch in diameter, produced by combustion as much light as 74 stearine candles. The light, therefore, arising from combustion, depends to a great extent on the nature of the combustible, as well as on the product of combustion. Substances like iron and charcoal, which are fixed, emit a great amount of light in proportion to the heat produced and the constant renewal of surface leads to continuous combustion.

The *intensity* of the light is, *cæteris paribus*, dependent on the rapidity with which oxidation takes place, and the amount of material consumed. The *Bude* light owes its brightness to the introduction of a current of oxygen into the centre of the flame. There is in a given time a larger consumption of the combustible matter, and a consequent increase of light.

The *color* of the light emitted in combustion, is to a certain extent, dependent on temperature. At one degree of heat, the light is red, at another yellow, and in the highest degree white. These three colors are well known in chemical processes as forming broad distinctions in the temperature of ignited solids (*see* page 96). According to Bunsen, between the yellow, red, and white heat, the colors of intensely heated bodies pass through shades of blue to violet, and the white heat is the resultant of all the spectral colors emitted by the heated substance. Apart from the effects of temperature, there are colors which are peculiar to the combustible substance. The light evolved by burning sulphur is of a pale blue color, while zinc gives a greenish white; potassium, a pale purple or violet; sodium, an intense yellow; lithium, calcium, and strontium, shades of red; barium, greenish yellow; boracic acid, green; arsenic, a violet blue; and antimony, a pale lemon color. It will be perceived, by reference to page 93, that the colors which are thus produced during combustion, differ from those which are emitted as a result of the incandescence of the same bodies.

Among the compound gases, carbonic oxide is known by the blue color of its flame; cyanogen gas by a violet flame with a blue halo; and phosphuretted hydrogen gas by the intense yellowish-white light which it emits during combustion.

Nature of Flame.—Flame arises from the combustion of volatile or gaseous matter emanating from the heated solid. Those bodies only burn with flame which at the usual burning temperature, are capable of assuming the vaporous or gaseous state. Charcoal and iron burn without flame; their particles are not volatile at the temperature at which they burn. Phosphorus and zinc, on the other hand, are volatile bodies, and therefore burn with flame. Small particles of each substance are carried up in vapor, are rendered incandescent by the heat of combustion, and burn wherever they meet with the atmospheric oxygen; the more volatile the substance, the greater the amount of flame.

Flame is hollow—a fact which may be proved by numerous experiments. If a piece of metallic wire-gauze be depressed over a flame, this will be seen to form a ring or circle of fire, dark in the centre and luminous only at the circumference, where the gaseous particles meet with oxygen. The inflammable matter traverses the meshes of the gauze, but is so cooled by the conducting power of the metal that it ceases to burn above. A piece of stiff paper suddenly depressed on a spirit-flame to about its centre, presents a carbonized ring corresponding to the circularity of the flame. If a thin platinum wire be stretched across a wide flame of alcohol, it will be heated only at the two points, corresponding to the circumference, where combustion is going on.

By allowing a jet of gas to issue from a glass cylinder, in the manner described at page 94, a variety of experiments may be performed to show the hollowness of flame, and the comparatively low temperature of the gas or vapor in the interior. A lighted wax taper fixed on wire, introduced suddenly through the sheet of flame, is extinguished in the interior. Gunpowder introduced in a ladle may be held in the inner space within the flame for a long time, and even withdrawn without exploding. Gun-cotton will not explode under these circumstances if introduced at the end of a copper wire, while the coal-gas is freely issuing from the chimney-glass, and the jet is not kindled until after its introduction. That the inner portion of every cone of flame consists of unburnt gas, or combustible vapor comparatively cool, may also be proved by placing within it the open end of a glass tube, supported by wire, and applying a lighted taper at the other end of the tube which projects out of the flame. The unburnt gas or vapor will be conducted off by the tube, and may be kindled at the end of it, as from an ordinary jet. Thus, then, all inflammable gases and vapors, when unmixed with oxygen, have only a surface combustion, which is defined by the access of oxygen and its contact with the heated gas or vapor.

Flame in all cases consists of matter ignited to a high temperature. Sir H. Davy assigned a white heat to ordinary flame. Bunsen has recently examined the temperature of flames by a series of ingenious experiments (*Phil. Mag.*, Aug., 1860, page 92), and has arrived at the following conclusions: the temperatures here assigned, being those of the centigrade thermometer, of which 5° are equal to 9° of Fahrenheit, plus 32° for the difference of the zero.

Sulphur flame . . .	1820°	Carbonic oxide flame . .	3042°
Sulphide carbon . . .	2195°	Hydrogen flame (in air) .	3259°
Coal-gas flame . . .	2350°	Oxyhydrogen flame . .	8061°

The heat of the electric flame far surpasses all these temperatures, and is at present undeterminable in its degree by any known process.

A remarkable announcement has been made by Kirchoff and Bunsen, respecting the colored flames of metals brought to the state of incandescent vapor, as the result of the heat of combustion or of the electric current—namely, that they absorb light of the same degree of refrangibility as that which they emit; in other words, their flames are opaque to their own light. If the light of the sun, or of the electric current, is allowed to traverse the flame of a spirit-lamp or that of hydrogen or coal-gas, no shadow is produced on a white screen placed behind it: the flame is quite transparent, but the undulating shadows projected for more than a foot above the flame by the invisible gaseous products of combustion (carbonic acid and water), are plainly seen. The flame of a common candle produces no shadow when placed between a screen and the flame of an oil-lamp. The shadow of the wick only is seen on a white surface. Foucault observed that the intense light of the electric arc from carbon-points, was so transparent that the solar rays converged upon it by a lens, completely traversed it, and only a slight shadow was cast upon the solar light. Bunsen found that the light of a sodium-flame would not traverse another sodium-flame, or even sodium-vapor, produced by heating sodium-amalgam in a test-tube much below its point of luminosity; and the singular discovery was made, that direct sunlight, passed through the yellow flame of sodium, changed the yellow spectral band peculiar to that metal to a dark double line. The red band of lithium was also changed to a dark band by sunlight. (*Phil. Mag.*, August, 1860, page 108.) From these results, and from the fact that in the pure solar spectrum, a dark line appears in the position of the sodium-yellow band, Kirchoff and Bunsen have inferred that sodium must be a large constituent of the photosphere of the sun. For a similar reason, chromium, iron, nickel, and magnesium have also been assigned to this photosphere—and sodium to the light of the fixed stars. The moon and Venus exhibit lines corresponding with those of the sun. Sirius showed different lines, and Castor others which were again different. In Procyon the solar line D (sodium), and in Capella and Betalgeux, the principal star in Orion D (sodium) and b were found. (Miller.) It is to be observed, however, that the light of platinum, rendered incandescent by the electric fluid, and the rays of a Drummond light, equally changed the sodium-yellow into a dark band. Opacity is the great character of metals: but it is remarkable that, in the state either of incandescent or non-luminous vapor, this complete opacity to light emitted by their own flames, should thus exist. If these results are confirmed, this property of metallic vapors might be made a test of the alleged metalline nature of certain gases. Incandescent hydrogen gives colored spectral bands of its own (page 59); but these have not been found to possess any absorbent power at ordinary temperatures. This result is adverse to the hypothesis of its metalline nature.

Products of Combustion.—The products of ordinary combustion in oxygen are chiefly *water* and *carbonic acid.* They are quite unfitted to sustain combustion, and unless removed as they are produced, they speedily arrest the process.

Combustion by Oxygen Salts.—Deflagration.—It is not necessary that oxygen should be in the free or gaseous state, in order that combustion should take place. Salts which abound in oxygen, such as the alkaline perchlorates and chlorates, nitrates and bichromates, when mixed with substances which have a tendency to unite with oxygen—*e. g.*, charcoal, sulphur, or phosphorus—and heat is applied to the mixture, give rise to combustion of a most intense kind. The salts above mentioned, contain a large proportion of oxygen by weight, and this is readily evolved in contact with a combustible. Even the liquid acids of these salts, in a free state, are capable of producing the phenomena of combustion. Dr. Roscoe found that pure perchloric acid, obtained from the perchlorate of potash, was a most powerful oxidizing agent. A single drop of the liquid brought into contact with charcoal, paper, wood, alcohol, or other organic substances of the like nature, caused combustion with explosion, falling not short in violence of that of chloride of nitrogen.

The sudden conversion of gunpowder into gaseous and vaporous matter is dependent on the oxygen of the nitre combining at a high temperature with the charcoal and sulphur. Gun-cotton contains nitrous acid in large proportion. This readily parts with its oxygen at a moderate heat, and the carbon and hydrogen of the cotton are entirely consumed. If a quantity of nitre is melted in a flask, and a piece of red-hot charcoal is dropped on the melted salt, it will continue to glow as a result of combustion, at every point at which it touches the nitre, until all the charcoal or the nitre has been consumed. If chlorate of potash is melted in a flask, and a piece of lighted wood is introduced into the liquefied salt, there is violent and intense combustion, almost amounting to explosion. A mixture of finely-powdered charcoal, with an equal portion of powdered nitrate or chlorate of potash, burns, when heated, with great violence, giving rise to the phenomena of *deflagration.* This process of combustion is occasionally resorted to by chemists for oxidizing carbon, sulphur, and phosphorus in organic substances, in order to convert the elements to salts, and determine the presence and proportion in which they exist. A mixture of twenty-eight parts of ferrocyanide of potassium, twenty-three parts of white sugar, and forty-nine parts of chlorate of potash, is known under the name of "*white gunpowder.*" In combustion it produces a large amount of gaseous matter, consisting of nitrogen, carbonic acid, carbonic oxide, and aqueous vapor. This is a dangerous compound to prepare or even to preserve. The materials should be separately powdered, and then mixed. Mr. Hudson has observed, that when the materials are ground together with a little water and dried at 150°, the powder is much more explosive. Even simple friction with a spatula, or slight compression, was then sufficient to cause a violent explosion. A drop of sulphuric acid will explode it; it may also be exploded by percussion. This chemist found that its explosive force was twice as great as that of common gunpowder. (*Chem. News*, Aug. 24, 1861.) It would prove a dangerous substitute for gunpowder, but it might be serviceable as a composition for shells. An explosive mixture is also formed by powdering separately, and mixing, two parts of the black sulphide of antimony with one part of chlorate of potash. This composition, when dry, is exploded by friction or percussion, by heat, or by the contact of concentrated sulphuric acid. It furnishes an instance of violent combustion, at the expense of the oxygen of the chloric acid.

CHAPTER VIII.

OZONE.—ALLOTROPIC OXYGEN.—ANTOZONE.

History.—In addition to the ordinary state in which oxygen is known to chemists, it is believed to exist in another state—that of *allotropic oxygen,* or, as it is generally called, OZONE. It had been noticed that a peculiar pungent odor, resembling that of phosphorus, was sometimes evolved on the discharge of the electric spark—that litmus paper was reddened—that starch-paper moistened with iodide of potassium was rendered blue; and that paper moistened with potash, deflagrated when dry. These effects were generally referred to the production of nitric acid by the oxidation of the nitrogen of the air. In 1840, Schönbein of Bâle announced that in the electrolysis of water, this odorous body appeared at the positive pole of the battery (if of platinum) and that it might be preserved in well-closed bottles. He considered it to be an electro-negative element, and named it Ozone (from ὄζω to smell). In the *Comptes Rendus* for 1850, he described a method of procuring it from phosphorus and ether, as well as its most characteristic properties; and announced that it was produced in the atmosphere, especially during winter, as the result of electrical changes.

In a lecture at the Royal Institution, in June, 1851, Mr. Faraday gave an account of Schönbein's researches, with the results of his own observations. Fremy and Becquerel in France, and Dr. Andrews and Dr. Tait in this country (*Phil. Trans.*, 1855–6) have since investigated the subject. [The reader is also referred to an Essay by Dr. Scoutetten, entitled *L'Ozone, ou l'Oxygène électrisé.* Paris, 1856; and for a more recent account of Ozone in its medical aspects, to a Paper by Dr. Moffat, read at the British Association Sept. 1861.

The results obtained by different observers tend to show that ozone is oxygen in an altered state; and that this conversion may be produced by the electric spark (when silently emitted)—by current electricity in the decomposition of water, and by various chemical processes; further that however produced, the properties are the same. The principle evolved is characterized by a peculiar odor, and by an intensely oxidizing and bleaching power—so that substances on which common oxygen produces no effect, are rapidly oxidized on contact with air which contains only a small portion of this odorous principle.

Preparation.—The most convenient method of procuring ozone, or rather an ozonized atmosphere, is to place in a large bottle of air, which can be completely closed, a stick of *phosphorus* freshly scraped. Sufficient distilled water should be poured into the bottle to partially cover the phosphorus; the vessel should then be closed with the stopper, and kept in a room at a temperature between 60° and 70°. The phosphorus is oxidized in the bottle in the usual way; and during this process of oxidation, a portion of the oxygen passes to the state of *ozone*, and is diffused through the air of the bottle. The test for its presence is a slip of paper moistened with a solution of starch and iodide of potassium. (*See* page 104.) When ozone is produced, this paper, on immersion, acquires a blue color, owing to the oxidation of the potassium and the production of iodide of starch. If a similar slip of paper is put into a similar bottle of air, containing distilled water without phosphorus, no change is produced. In a warm room, the evidence of the presence of ozone in the bottle is usually procured in about ten or twelve minutes; but the maximum quantity of ozone is found in it in from two to ten hours. Only a small part of the oxygen (from 1-50th to 1-200th) appears to undergo this change; and if long kept, the ozone may be lost by combining with and oxidizing the phosphorus. So if the iodide-paper be left in the bottle, the blue color will after a time disappear, by the ozone combining with the iodine to form iodic acid. It is not produced in dry oxygen, nor in humid air, or in oxygen mixed with certain gases or vapors which prevent the oxidation of phosphorus; but it appears to be more readily produced, *cæteris paribus*, when oxygen is mixed with nitrogen, hydrogen, or carbonic acid. By washing and decantation, the ozonized air, which is quite insoluble in water, may be deprived of the phosphorus-vapor associated with it, and kept in well-closed bottles. It is speedily lost by diffusion. Graham found that ozone traversed dry and porous stoneware. Ozone may be produced on a small scale, by placing a piece of phosphorus with water in a watch-glass and inverting over this, another glass containing the test-paper or liquid.

Ozone is produced by passing the electric spark silently into pure and *dry* oxygen. Fremy and Becquerel found that pure oxygen, contained in a sealed tube, when treated for a sufficient time with a series of electric sparks, underwent a complete conversion into ozone, as the whole contents of the tube when broken were absorbed by a solution of alkaline iodide, in which it was immersed. In the electrolytic decomposition of water the oxygen at the positive pole has ozonic properties, provided the poles employed are of gold or platinum. The hydrogen evolved gave no indication of ozone. Faraday found that a mixture of iodide of potassium and starch was decomposed at the positive pole, even after the gaseous oxygen had been made to pass through a tube containing a layer of cotton soaked in a solution of potash. The object of this arrangement was to arrest any acid which might be simultaneously produced, and thus lead to the decomposition of the iodide. Dr. Letheby found that the ozone thus evolved at the positive pole possessed the same power of coloring strychnia or aniline as the oxygen (ozone) liberated by sulphuric acid from the peroxides of manganese and lead, and from chromic acid.

In 1850, Schönbein found that ozone was a product of the slow combustion of *ether.* If a small quantity of ether is poured into a jar or bottle, and a clean glass rod, or small iron poker, heated to about 500°, is introduced, acid vapors are given off which redden wetted litmus paper at the mouth of the jar, and which set free iodine from iodide of potassium, causing the blueing of starch-paper impregnated with this salt. After the removal of the rod or poker, several strips of paper successively introduced into the jar will undergo the same change. Clean platinum, and even copper, will produce similar effects. The residuary ether in the jar at the same time acquires new properties. It bleaches sulphate of indigo, and converts chromic into blue perchromic acid (owing to the presence of antozone or peroxide of hydrogen).

If the rod or metal used in this experiment is too strongly heated, the ozone formed is reconverted into oxygen; and if it is not sufficiently heated, no ozone is produced. In either case the tests fail to show the presence of an oxidizing body. It has been suggested that the results of this experiment are explicable on the supposition that the nitrogen of the air is burnt, or oxidized at a low temperature, and converted to nitric acid; but the fact that they are not observed at temperatures at which ozone cannot, and nitric acid can, exist; and further, that the ether itself undergoes changes which admit of no explanation on this hypothesis, are circumstances adverse to this view. As a permanent source of ozone, Boettger has recently suggested that a mixture should be made of two parts of permanganate of potash and three parts of sulphuric acid. The pasty mass thus produced will, he states, continue to give off ozone for several months. (*Chem. News*, Aug. 1861.) The effects in this case have been referred to the presence of chlorine. (*Chem. News*, Oct. 26, 1861.)

Properties.—It has been found that in whatever manner ozone is produced its properties are the same. It is insoluble in water, alcohol, and ether. When much diluted with other gases, it is destroyed by agitation with a large quantity of water. It is readily dissolved by a solution of an alkaline iodide, converting it to iodate, and it is absorbed by leaf silver in a humid state. It decomposes the protosalts of manganese (sulphate and chloride), producing peroxide, and causing a brown stain on paper immersed in these solutions. Silver leaf, on which common oxygen has no action is, when wetted and exposed to ozonized air, slowly oxidized, and the ozone disappears. Andrews found that *dry* silver, whether in leaf or filings, entirely destroyed ozone when prepared by electrolysis or by frictional electricity, and that mercury had also the property of absorbing it. Thin films of metallic arsenic and antimony are oxidized by it—the arsenic is rapidly converted into arsenic acid and disappears. This experiment, which seems to distinguish a deposit of metallic arsenic from one of antimony, may be thus performed. Place a watch glass, containing the deposit of arsenic, over another containing a clean slice of phosphorus with a few drops of water. In a few hours the arsenical deposit will entirely disappear. Peroxides of manganese, silver, lead, and iron, as well as oxide of copper, destroy it, or rather convert it to oxygen. Among other reactions, the sulphides of lead and silver are changed into white sulphates, and cyanide of potassium into cyanate of potash, while the yellow ferrocyanide is converted by it into the red ferricyanide of potassium.

Organic substances are variously affected by it. Vegetable colors are bleached or altered. Blue litmus is bleached without being first reddened. The color of sulphate of indigo is discharged when the liquid is shaken with ozonized air. Filtering-paper, soaked in aniline or pyrogallic acid, is rapidly turned brown. Andrews found that caoutchouc and cork are rendered brittle and destroyed. Besanez noticed that uric acid in water, when shaken with ozonized air, was dissolved and changed into urea and allantoin. (*Rép. de Pharm.*, 1859, and *Chem. News*, 1, 37.) He also found that ozone readily entered into combination with tannic acid, and that oxalic acid was a product of this union.

All these chemical changes are due to oxidation; and *oxides* alone result. In many respects ozone resembles chlorine. It readily displaces hydrogen, oxidizing it as well as the radical with which it is associated. It will even combine with nitrogen at common temperatures, when in contact with water and a base. Ozonized air, placed over lime-water, produced nitrate of lime, and from this compound, nitre was procured by double decomposition (Schönbein). It oxidizes ammonia, and sulphuretted hydrogen gas, and converts nitrous and sulphurous, into nitric and sulphuric acids. It acts as a powerful disinfectant, and its influence in the atmosphere, is considered to be exerted in oxidizing and destroying foul effluvia. It is at any rate difficult to procure evidence of the presence of ozone in the vicinity of these effluvia, or in densely populated places; and it is equally difficult to understand how ozone in a free state, can be to any extent diffused through the atmosphere, when its tendency to combine with all oxidizable substances is proved to be so powerful.

Although ozone is not soluble in water, it appears to be dissolved by certain liquids. The oils of turpentine and cinnamon, which have been kept for a long time in contact with air, contain it in such quantity that they possess remarkable bleaching powers. Ozone is a constituent of the alkaline permanganates, and when these are dissolved in water it exists potentially in a state of solution. The destruction of the pink color of the permanganate of potash by organic matter, is probably owing to the separation of the oxygen as ozone. One drop of a solution of the permanganate added to a mixture of iodide of potassium and starch, produces the blue iodide of starch by oxidizing the potassium. Sulphate of indigo is bleached by this liquid, and foul effluvia are oxidized and lose their offensiveness. An alkaline permanganate, under the name of *ozonized water*, has been of late much used in medical practice as a deodorizer. The peroxide of manganese—one of the class of *ozonides*, presents similar properties. The peroxide has no action on a solution of iodide of potassium and starch; but if a little acetic acid is added, oxygen, as ozone, is set free, and the liquid immediately acquires a blue color. If diluted sulphate of indigo is substituted for the alkaline iodide, the color is discharged. The compounds containing oxygen as ozone are called, by Schönbein, *ozonides*. The following are the principal:—

Mn_2O_7	PbO_2	CrO_3	Co_2O_3	MnO_3
$Mn\,O_2$	AgO_2	BiO_5	Ni_2O_3	

Among these, peroxide of lead appears to have a most energetic action. Without the addition of any acid, it instantly sets free iodine from iodide of potassium, and bleaches a solution of sulphate of indigo. When one part of dry sulphur is rubbed in a warm mortar with five or six parts of dry peroxide of lead, the oxygen, as ozone, is suddenly given off with combustion of the sulphur, and formation of sulphide of lead.

Mr. Spencer enumerates the magnetic oxide of iron as one of the compounds of this metal, containing oxygen in the state of ozone. He has constructed a filter in which this mineral substance is the active material for the purification of water, by oxidizing and destroying all organic matters contained in it.

One of the most remarkable properties of ozone is, that from whatever source it may be derived—it is reconverted into oxygen by a moderate heat. If the heat be between 500° and 600°, the conversion is immediate; at a lower temperature (450°) it takes place more slowly. Andrews found that no water was produced during this conversion, and that only pure oxygen resulted. Fremy and Becquerel have confirmed this result. This disposes of the question, whether ozone is a higher oxide of hydrogen. It obviously contains no hydrogen. Ozonized air passed through a tube heated as above mentioned, produces the usual reaction on iodide paper on entering the tube, but has entirely lost this property when it passes out. Hence, while electricity converts oxygen into ozone—heat reconverts ozone into oxygen. Electricity, in long-continued sparks, will also bring about this reconversion into oxygen. Faraday has proved by experiment that when electrical discharges are made through a heated platinum coil, no ozone is produced, while, when the coil was allowed to cool, ozone reappeared with each spark. These facts show not only that ozone is oxygen; but also that the oxidizing effects attributed to it in the various modes of its production cannot proceed from the presence of nitric acid, hyponitric acid, or chlorine. A heat of 500° would not destroy the oxidizing action of these compounds.

When peroxide of manganese is heated, oxygen is said to be given off; but ozone may, in this case, be evolved, and converted into oxygen by heat. (Schönbein.) Peroxide of manganese, iron, and lead, absorb ozone, and convert it into oxygen at all temperatures. When either of these compounds is mixed with chlorate of potash, and heated, it is well known that oxygen is obtained from the chlorate at a much lower temperature than when the oxide of manganese or chlorate is separately heated; but no oxygen is evolved from the peroxide (*see* page 81). Schönbein explains this singular phenomenon by assuming that the chlorate is a compound of chloride of potassium and of oxygen as ozone; and that this combined ozone, like free ozone, is changed by the peroxide to oxygen, and is thus readily separated from the chloride. The oxygen thus obtained, always contains chlorine. It has the odor of this gas, bleaches litmus paper, decomposes iodide of potassium, and precipitates a solution of nitrate of silver. It is probable that, in this case, the ozone displaces a portion of the chlorine from the chloride, and that some manganate of potash is formed.

Peroxide of iron has even a more powerful effect by contact with the chlorate. A thousandth part of the peroxide mixed with the fused chlorate, was found to liberate oxygen abundantly; and with one two-hundredth part, the oxygen was evolved with great rapidity—the saline mass becoming incandescent. A mixture of one part of peroxide with thirty parts of chlorate, when heated to the point of fusion, brought about an ignition of the mass with an evolution of the gas almost amounting to explosion. (Pelouze et Fremy, *Op. cit.* 1, 194.) In this case, also, chlorine is set free, and probably some ferrate of potassa is formed.

Tests.—Various methods are employed for testing the presence of ozone in a gaseous mixture containing it. The iodide of potassium and starch elsewhere referred to (page 101), is generally employed, and is known as Schönbein's test. It is thus prepared: One part of *pure* iodide (free from iodate) is dissolved in two hundred parts of distilled water; ten parts of starch, finely powdered, are mixed with the solution, and the liquid is gently heated until it is thickened from the solution of the starch. White unsized or sized paper is soaked in the liquid: the paper is dried, cut into slips three inches long by three quarters of an inch wide, and these are preserved in a stoppered bottle.

When intended for use, a slip of the prepared paper is exposed to a free current of air in a spot sheltered as much as possible from rain, light, and foul effluvia, for a period varying from six to twenty-four hours. An ingeniously constructed box has been contrived by Mr. Lowe for testing the atmosphere (*Proc. R. S.*, vol. 10, p. 531). By exposure, the paper becomes brown, and when wetted acquires shades of color, varying from a pinkish white and iron gray to a blue. A chromatic scale, covering 10°, has been contrived by Schönbein, with which the changes in the wetted paper may be compared. Fremy recommends, as a test, white blotting-paper, soaked in an alcoholic solution of guaiacum, and dried in the dark. By exposure to an ozonized atmosphere this paper acquires a bright blue color. Houzeau's test is a strip of litmus paper of a wine-red color, of which one-half has been soaked in a solution of iodide of potassium in water, in the proportion of one per cent. As a result of exposure to ozonized air, the iodized portion becomes alkaline, and the paper acquires a deep blue tint. The other portion preserves its normal color; and by showing an acid or alkaline reaction, may reveal the presence of vapors in the air, which might otherwise be a source of error.

As paper is fragile, slips of clean calico (containing starch), dipped in iodide of potassium, have been substituted by Mr. Lowe. This gentleman found that twenty-four hours' exposure was required for a satisfactory result. The calico may be used dry, and wetted after the exposure is complete. The iodized calico acquires various shades of a brown color, becoming pink, gray, or blue, when dipped in water. Mr. Lowe observed that the strongest effect was produced during the night, and at some elevation above the ground; also that the months of January, February, and March, gave the largest amount, both day and night. On a great number of days on which observations were made, there were no visible traces of ozone. Other observers have found it to vary according to locality, the season of the year, the hour of the day, the direction of the wind, and the height of the place above the level of the sea. It is seldom found in closely inhabited spots. In some observations made at Brighton, Mr. Faraday procured evidence of ozone on test-paper exposed to a current of air from the sea, close to the sea-shore, as well as in the air of the open downs above the town; but none in the air of the town. Dr. Angus Smith could not detect ozone in the air of Manchester; but at a distance, it was easily recognizable when the wind was not blowing from the town. Some strips of paper, prepared by the process described (see above), were exposed in Southwark, and at Connemara, in Ireland. At the former place, there was no change in twenty-four hours; while at the latter, the paper acquired a brown color in a few hours; and on dipping it into water it became blue. It has been objected to this mode of testing, that the change in the alkaline iodide under these circumstances, may be due to chlorine, nitric, and other acids, or to organic compounds diffused in the atmosphere, and not to ozone. But it is to be observed, that the test-paper remains unchanged exactly in those spots where such compounds would be likely to exist (*i. e.*, in inhabited towns); while the chemical effect is observed to be at a maximum on open heaths, or downs, on the sea-coast, and on lofty elevations, where there is no conceivable source of such impurities in the air. It is possible, too, as M. de Luca has suggested, that the nitric acid, even if really existing in the air of those places, may itself be the product of the oxidation of nitrogen by ozone: and this may be the source of nitric acid, often found in rain-water, and even in the atmosphere (*Comptes Rendus*, and *Chemical News*, September 7, 1861, p. 136). The absence of any reaction for 118 days out of 365, and the greater effect by night than by day, in wet than in dry weather, and in winter than in summer, show that these phenomena are not due to the presence of such impurities in the air as those suggested. At the same time, the presence of a large quantity of iodate of potassa in the iodide used, may have been a fertile source of error. A discoloration of the paper may then be produced by such compounds as sulphurous acid and sulphuretted hydrogen.

Constitution.—Ozone has been proved to be oxygen in a changed condition. Andrews found that peroxide of manganese in absorbing it, underwent no sensible increase of weight, although as much as 0·9 gr. were apparently destroyed; no water was produced. Hence it was transformed to oxygen, merely by contact, and it could not have contained any hydrogen. In its production by electrolysis, he also noticed that the active oxygen was exactly equal to the entire weight of the ozone—and was therefore identical with it. (*Proc. R.S.*, vol. 7, p. 476.) When oxygen has been contracted in bulk by the electric spark in the production of ozone, peroxide of manganese restores it to its original volume (vol. 9, p. 608). In fact, the conclusion drawn by the writer, is in accordance with the results of Schönbein, Faraday, Becquerel, and others—that ozone, from whatever source derived, is one and the same substance, and is not a compound body, but simply *oxygen* in an altered or allotropic condition.

Antozone.—While ozone is considered to be active oxygen in a $-$ state or $\ominus$, antozone is active oxygen in a $+$ state or $\oplus$.

Antozone at present is only suspected to be a constituent of certain peroxides. Of these compounds, Schönbein has furnished the following list, under the name of antozonides:—

HO_2 Na_2O_3 SrO_2.
KO_3 $Ba\ O_2$

In its action on alkaline iodides and in its bleaching properties, antozone resembles ozone. The differences pointed out by Schönbein are not very well marked. An ozonide evolves chlorine with hydrochloric acid; gives a blue color to the precipitated resin of guaiacum, and turns aniline (on paper) brown. It does not produce peroxide of hydrogen. An ozonide (MnO_2), with sulphuric acid, produces a rich series of purple colors with strychnia. An antozonide (BaO_2) similarly treated does not. Although dealing with peroxides in both cases, the oxygen as it is evolved, must therefore be different in its properties. The oxygen of an ozonide or antozonide, produces effects which common oxygen does not produce; and it is further remarkable that these two oxygens, which appear to be in oppositely polar conditions, have the power of neutralizing each other on contact, and of evolving ordinary oxygen in a pure state. Thus, when permanganate of potash or peroxide of manganese is mixed with a solution of peroxide of hydrogen, oxygen gas with its usual neutral properties, is given off ($MnO_2 + HO_2 = MnO_2 + HO + O$). There is after the mixture, no evidence of ozone —of antozone or of allotropic oxygen in any form. If oxygen be thus constituted, it should follow that whenever ozone is produced, antozone must also be liberated. In a recently published paper, Schönbein has stated, that in the ordinary production of ozone by phosphorus and water, so soon as the ozone appears, peroxide of hydrogen (HO_2, or antozone) may be detected in the water in which the phosphorus is immersed. By agitating the phosphorus with the water, he found that this liquid acquired the property, which it possesses in common with ozone, of oxidizing potassium, and setting iodine free from the iodide. In his view, by mere contact with phosphorus, neutral oxygen is split or decomposed into two oppositely active conditions—the positive oxygen being absorbed by the water, to form peroxide of hydrogen, whilst part of the negative oxygen escapes, on account of its gaseous and insoluble nature, into the atmosphere above the phosphorus. The greater part, however, combines to form phosphorous acid, which, like phosphorus itself, can remain in contact with peroxide of hydrogen without abstracting its active oxygen. (*Chemisch. Cent. Blatt*, Jan. 1860, and *Chemical News*, Feb. 11, 1860.) When pure oxygen is converted into ozone by electricity, it is probable that antozone is also produced, and that by continuing the electric sparks, or increasing their intensity, these bodies are reconverted into ordinary oxygen. When ether-vapor and air are combined, at a heat below 500°, ozone is produced in the surrounding air, while antozone (peroxide of hydrogen) is dissolved by the ether, giving to it bleaching properties, and a power of peroxidizing chromic acid. The nearest condition to purity in which antozone has been yet found, is in peroxide of hydrogen, obtained by the substitution of hydrogen for barium in the peroxide of that metal. (See *Peroxide of Hydrogen.*) While this theory appears to account for many curious facts which have hitherto been vaguely referred to action by contact or presence, it fails to explain satisfactorily all the phenomena. In the ozonized air obtained by the oxidation of phosphorus, the antozone is held dissolved by the water; but the ozone in ozonized air may itself be converted to oxygen by mere heat above 500°; hence the presence of antozone to produce neutral oxygen is not always necessary. So the ozone evolved from mixtures of the peroxides of manganese and iron with chlorate of potash, is converted into oxygen by heat, without reference to the presence of antozone.

CHAPTER IX.

HYDROGEN ($H=1$).

History.—In the form of water and aqueous vapor, hydrogen is universally diffused over the globe. One-ninth part of this liquid by weight consists of hydrogen; and it is from this source that the gas is readily and abundantly procured. The name of the element is derived from the Greek ὕδωρ, water, and γεννάω, to produce. Hydrogen is held with such affinity by oxygen and other bodies, that it is not found in nature in the free state. Bunsen states that he found in it a mixture of gases, collected by him in 1846, from the volcanic district of Nimarfjall, in Iceland. It existed in the proportion of 45 per cent. Hydrogen is an important constituent of animal and vegetable matter, entering largely into the composition of flesh and woody fibre. In union with carbon, it forms a large number of gaseous, liquid and solid compounds, known as the class of hydrocarbons. Associated with carbon and oxygen, it is a constituent of inflammable substances, such as alcohol and ether. Hydrogen appears to have been first examined in a pure state by Cavendish in 1766 (*Phil. Trans.*, vol. 56, p. 44). Previously to this it had been confounded with several of its compounds, under the name of *inflammable air.*

Preparation.—The best method of procuring hydrogen is to place in a flask, provided with a bent tube ground to fit the neck—one part of granulated zinc, four to five parts of water, and one part of strong sulphuric acid. There is a brisk effervescence arising from the rapid escape of the gas. This should be reduced, if too violent, by the addition of more water. It is a singular fact that, the purer the zinc, the less energetic is the chemical action; and, indeed, pure zinc is scarcely affected by the acid. The gas may be collected in the ordinary water-bath. The first portions are always contaminated with air, and at least three times the capacity of the flask used, should be rejected before the gas is collected for experiment. To ascertain whether the hydrogen is quite free from air, a few bubbles may be passed into a jar containing deutoxide of nitrogen placed over the bath. If no red fumes are produced, the gas is sufficiently pure for collection. The chemical changes which take place may be thus represented, $SO_3,HO+Zn=ZnO,SO_3+H$. The hydrogen is entirely derived from the decomposition of water, and as the gas is scarcely dissolved by this liquid, it is readily collected in large quantity. A cubic inch, or rather more than half an ounce of water by measure, contains twenty-eight grains of hydrogen, representing 1350 cubic inches, or about five gallons of the gas. In place of a tubulated flask, a wide-mouthed bottle, provided with a funnel-tube for pouring in the acid, and a bent delivery tube for the escape of the gas, may be employed.

Other methods have been suggested for procuring hydrogen, but they are seldom resorted to. Thus, iron has been substituted for zinc, but the gas is much less pure, and has generally an offensive smell from its producing an oily volatile compound by uniting with the carbon of the iron; sulphuretted hydrogen and other impurities may also be present. 2. Hydrogen may be obtained by passing the vapor of water over iron-turnings or wire, heated to redness in a porcelain tube. In this case the iron is converted to magnetic oxide [$3Fe+4HO=Fe_3O_4$ (magnetic oxide) $+4H$]. 3. It may be obtained by introducing a ball of sodium or potassium, wrapped in paper, into a stout jar full of water, placed over the water-bath. Hydrogen is here evolved without the intervention of an acid, and an alkali is produced ($Na+HO=NaO+H$). The hydrogen of water may be set free by alkalies as well as by acids in their reaction on metals. Thus aluminum in a strong solution of potash liberates the hydrogen and appropriates the oxygen ($2Al+KO+3HO=Al_2O_3+KO+3H$).

As both zinc and sulphuric acid are frequently contaminated with arsenic and sulphur, hydrogen, as it is usually obtained, is very impure. The purity of the materials may be determined by generating the hydrogen in a bulb-tube, and passing the gas into diluted solutions of nitrate of lead and nitrate of silver. A brown discoloration of the lead indicates sulphur, while a brownish-black precipitate in the silver solution indicates arsenic, phosphorus, or antimony. In order to determine whether the impurity is in the zinc, some of the metal should be treated with sulphuric acid of known purity, and the gas thus produced separately tested. The presence of arsenic in hydrogen is a dangerous contamination; the poison is not only set free during combustion, but if the gas should be accidentally breathed, it may cause serious symptoms, and even death. A Dublin chemist lost his life a few years since by inhaling hydrogen thus contaminated with arsenic; the purity of the sulphuric acid had not been previously tested. The absolute freedom of hydrogen gas from arsenic, antimony, phosphorus, or sulphur, may be proved by introducing into a jar, with its mouth downward, a slip of filtering-paper, moistened with nitrate of silver. The paper should not be discolored in the gas, if pure.

In order to procure pure hydrogen, pure materials should not only be used, but the gas should be collected over mercury. Hydrogen may be freed from all the usual impurities by passing the gas, before collection, through two U-tubes, both containing broken pumice—in the one tube, impregnated with a solution of potash, in the other, with a solution of corrosive sublimate. In the first tube, the compounds of sulphur and carbon are separated, and in the second, those of arsenic and phosphorus. Hydrogen may be obtained perfectly dry by causing it to traverse a third tube containing chloride of calcium, after it has left the purifying apparatus.

The hydrogen liberated by the electrolysis of water from platinum surfaces (*see* WATER), may, when dried, be considered as absolutely pure. In this form, hydrogen has been employed by Mr. Bloxam for the separation of arsenic and antimony from organic liquids.

Properties.—Hydrogen is a gas which has not yet been liquefied by cold or pressure: it is not dissolved by water, unless that liquid has been previously deprived, by long boiling, of common air, in which case 100 cubic inches dissolve about 1·5 cubic inches of the gas. When perfectly pure it has neither an acid nor alkaline reaction, has no taste, and is inodorous; but as it is commonly made, it has a slightly disagreeable smell from traces of foreign matters associated with it. It may be respired for a short time, although it is fatal to small animals. It does not act as a poison, but causes death by suffocation, *i. e.*, by the exclusion of oxygen. As a substitute for nitrogen in atmospheric proportions with oxygen, it has been breathed for some time without any other effect than that of producing a slight tendency to sleep. The intensity of sound is greatly diminished in an atmosphere of hydrogen. Leslie, indeed, found that the sound was more feeble than the rarity of the gas, compared with air, would have led him to expect. He placed a piece of clock-work by which a bell was struck every half minute, under the receiver of the air-pump, and, after exhausting the air, filled the receiver with hydrogen; but the sound was then even feebler than in the highly-rarefied atmosphere. (*Ann. Philos.*, 2d Series, 4, 172.) It is stated that sound moves at least three times as fast in hydrogen as in air.

Hydrogen gas is the lightest known form of matter. It is 14·4 times lighter than air, and 11,000 times lighter than water. In consequence of its extreme lightness, it is difficult directly to determine its weight with accuracy by the common process; but the researches of Berzelius and Dulong, and of Dr. Prout, lead us to infer that its specific gravity, compared with oxygen, is as 1 to 16: 100 cubic inches, therefore, of pure hydrogen gas at mean temperature and pressure weigh only 2·14 grains, and, compared with air, its specific gravity would be nearly as 7 to 100, or more correctly as 0·0691 to 1. Boussingault and Dumas have shown that the density of hydrogen is between 0·0671 and 0·0695. (*Ann. Ch. et Phys.*, 3d series, 8, 201.) At a temperature of 32°, 100 cubic inches weigh 2·22756 grains. (THOMSON.) It has the highest refracting power of all the gases. Compared with air it is 6614 to 1000. In relation to magnetism, it was found by Faraday to be diamagnetic; a vacuum being 0·0, hydrogen was 0·1. In the magnetic field, a tube containing it assumed an equatorial position, or pointed east and west. Its specific heat, compared with an equal weight of air, was 12·340 to 1000. In its electro-chemical relations hydrogen is strongly positive, and in electrolysis always appears at the negative pole. It displaces the metals under these circumstances, and enters into combination with the oxygen or salt-radical. This is one of the facts which is considered to favor the hypothesis that hydrogen itself is the gaseous state of a metal permanently volatile at the lowest temperature.

The low specific gravity of hydrogen may be illustrated by substituting it for common air, in soap-bubbles, which then rapidly ascend in the atmosphere, and may be kindled by the flame of a taper. This property led to its employment formerly in the inflation of balloons, but of late years coal-gas has been substituted. Small balloons, made of gold-beater's skin, or of collodion, when filled with pure hydrogen, dried by passing it through a tube containing chloride of calcium, rise in the air, their specific gravity being inferior to that of the surrounding atmosphere.

Hydrogen is inflammable, and extinguishes flame. When pure, it burns quietly, with a pale yellowish flame at the surface in contact with air; but, if mixed with twice its volume of air, it burns rapidly, and with detonation.

The phenomena of its combustion vary according to the mode in which the experiment is performed, but the product is always water (HO)—the hydrogen at a high temperature taking the oxygen from the atmosphere. If, by withdrawing the glass plate from a jar, a slight aperture only is made, the gas may be kindled without explosion, and by the gradual withdrawal of the plate, it will burn quietly, and with a scarcely visible flame, until all is consumed. If the gas is kindled, as the cover is suddenly removed, it always burns with explosion by its rapid admixture with air in its great tendency to diffuse. If the cover be entirely removed, and the lighted taper be held six or eight inches above the mouth of a jar, there will be an interval before combustion takes place, and the gas will then burn with a loud explosion. The following experiment may serve as another illustration. Drop a piece of potassium into a stout jar containing hydrogen gas, having a stratum of an inch of water at the bottom. The potassium at first decomposes the water without producing flame; but, in a few seconds, the air rushes in to supply the place of a portion of the hydrogen which has escaped, and the mixture is then kindled by the burning potassium with a loud detonation. This experiment may be performed with perfect safety in a stout glass jar, eight inches deep and two or three inches wide. It illustrates the decomposition of water by a metal, and its recomposition by the union of its elements at a high temperature.

It has been stated that hydrogen extinguishes burning bodies; in other words, that it does not support combustion. To prove this, the jar containing the hydrogen must be inverted. A large jar filled with the gas, having its open end downwards, may be brought over a lighted taper, supported on a wire. The gas is instantly kindled, and burns at the mouth of the jar. By depressing the jar over the taper this will become extinguished, and the blackened wick will be seen in the midst of the hydrogen, which is burning below. The taper may be relighted by raising the jar, and again extinguished by depressing it, an experiment which may be repeated several times. There are other interesting experiments which prove that hydrogen is not a supporter of combustion in the ordinary meaning of these terms. Place a piece of phosphorus in a small saucer floating in a vessel containing a thin stratum of water. Kindle the phosphorus, and, when fully burning, cover it completely with a jar of hydrogen as with an extinguisher. The hydrogen is inflamed at the mouth of the jar, but, with the flame of the phosphorus, it is extinguished when the jar is plunged beneath the water. In place of phosphorus, a piece of camphor may be employed with like results. Paper impregnated with a solution of nitrate of potash, when dried, ignited, and introduced into a jar of hydrogen, is extinguished. A certain degree of heat is required for the kindling of this gas in air. It is not inflamed by an iron bar heated to dull redness, but is immediately kindled at a bright red heat.

During combustion, hydrogen combines with eight times its weight of oxygen, producing a more intense degree of heat, weight for weight, than any other combustible. (*See* page 95).

Hydrogen, when mixed with air, and inflamed by a taper or the electric spark, burns with a loud explosion. Cavendish found that the loudest explosion was produced by mixing one volume of hydrogen with three of air, or two volumes with five of air. One of hydrogen with nine of air burned very feebly, and four of hydrogen with one of air burned without explosion. (*Phil. Trans.*, 56.) If, instead of employing a mixture of hydrogen and atmospheric air, two volumes of hydrogen are mixed with one of oxygen, and inflamed in a stout jar, the explosion is extremely violent; but if the mixture be diluted with eight measures of hydrogen, or with nine of oxygen, it no longer explodes. The cause of this violent explosion is owing to the sudden conversion of a large volume of mixed gases to liquid water by condensation. As 528 cubic inches of mixed gases produce only 0·4 cubic inch of liquid water at 60°, there is a diminution in volume to $\frac{1}{2000}$th part. A vacuum is thus produced, into which the air suddenly rushes, producing a loud sound. There is, however, in the first instance, expansion by the effect of heat, and this is instantly followed by a condensation of the produced steam or aqueous vapor.

The inflammability and low specific gravity of hydrogen are shown in the following experiments: Let a jar filled with this gas stand for a few seconds with its mouth upwards; on introducing a lighted taper, the gas will be found to have escaped, and to have been replaced by common air. Place another jar of the gas inverted, or with its mouth downward; the gas will now be found to remain a much longer time in the jar, being prevented from escaping upwards by the bottom and sides of the vessel. A jar of this gas may, for the same reason, be removed with its mouth downwards from the water-bath without a cover, and thus transported to a considerable distance. It may then be inflamed and burnt, by bringing the open mouth over a lighted candle. Place a bell-jar having a narrow neck and containing hydrogen, so that the wide open end may rest on three cubes. The jar may be removed from the bath, as in the previous experiment, without any cover. Remove the stopper and ignite the gas. It will burn with a fierce flame as the hydrogen is forced through the neck by the pressure of the external air beneath, and it will finally produce an explosion, but without any danger, owing to the last portions of the gas being mixed with the air in explosive proportions. If a piece of paper dipped in a solution of nitre and dried, is burnt under the mouth of a jar of hydrogen, it will be found that the smoke produced will float in a cloud below the gas, owing to the lightness of the hydrogen. A jar of air held over another containing hydrogen, from which the cover is then removed, will catch the hydrogen as it ascends. The application of a lighted taper will show its presence in the upper jar and its absence in the lower jar, in which it was originally contained. Hydrogen may, in fact, be decanted, as it were, *per ascensum*, from one jar into another held above it. Thus, if a light bell-glass be suspended with its mouth downwards to one end of a scale-beam, and accurately counterpoised, it will be found, on placing a jar of hydrogen gas (closed by a plate of glass) underneath it, that the hydrogen, on removing the glass plate, will ascend into the bell, and by its lightness cause the counterpoise to sink; the hydrogen may afterwards be inflamed by a taper introduced into the counterpoised bell. A large bell-glass, suspended, may be filled with hydrogen by displacement—*i. e.*, by opening one or two large jars of the gas beneath it, and allowing the hydrogen to ascend. If a bell be struck with a hammer in this atmosphere of hydrogen, it will be at once perceived how much the ordinary sound is reduced. A small shade, mounted on a handle, and introduced into this atmosphere of hydrogen, with its mouth downwards, will, after a few minutes, be filled with hydrogen by displacement. This may be transported to a distance, and kindled over a flame. The gas, owing to the admixture of air, will burn with a slight explosion.

If hydrogen is generated in a bottle, provided with a glass tube drawn out to a capillary point, it may be burnt in a jet at the end of the tube (*the Philosopher's lamp*); but care should be taken not to insert the cork with the jet until all the air has been removed from the bottle by the free escape of the gas. The hydrogen burns at first with a long pointed yellowish flame, which may be proved to be hollow like other flames (*see* p. 98). Although the light is feeble the heat is intense. Fine platinum wire is made white hot in an instant, and sometimes melted. Fine iron wire is rapidly consumed by combustion with the surrounding air, and glass is speedily melted. If a cold glass vessel be brought over the flame, the interior is speedily covered with the condensed vapor of water—the result of combustion; and, by a condensing tube, the water thus generated may be easily collected and tested. If, while the gas is burning, a tube from half an inch to two inches in diameter, and twelve to twenty inches long, open at both ends, be brought gradually over the flame, the flame becomes elongated, acquires a bluish tint at the mouth of the jet, and a peculiar sound is heard, varying according to the diameter of the tube. This forms what has been called a chemical harmonicon or hydrogen music. It arises from the vibration of the column of air within the tube, produced as a result of a rapid succession of slight explosions during the combustion of the gas. The tone varies in pitch with the length and diameter of the tube; and singular effects may be produced by employing for the experiment the tube of a broken retort. If, while the sound is issuing, a tube of larger size is placed at different heights over the tube in which the hydrogen is burning, there will be remarkable modifications of the sound. A small flame is better fitted for the production of this phenomenon, but, if too small, the flame may be extinguished by the strong current of air passing through the tube.

We may make use of this flame for the purpose of testing the purity of the gas. If a piece of cold glass or white porcelain be suddenly depressed on the point of the flame, and the gas is pure, there will be no stain or deposit. Nothing but a film of water will be perceived. If there be the smallest trace of arsenic or antimony in the gas, there will be a brown or blackish stain, more distinctly visible on the surface of porcelain than on the glass. By bending the tube at a right angle, and applying a strong red heat, by means of a spirit-lamp, to the horizontal portion, the presence of any foreign matters will be revealed. All the gaseous compounds of hydrogen are decomposed at a full red heat;—the gas passes off, and the solid impurity is deposited in a cold part of the tube. In this way the presence of the minutest traces of sulphur, arsenic, antimony, phosphorus, or selenium may be detected. A film or ring of the substance, recognizable by its color or metallic lustre, will be perceptible. As a proof of the facility with which hydrogen combines with these contaminating substances, it may be mentioned that when the pure gas is allowed to pass through a connecting piece of vulcanized rubber tubing, it will combine with a portion of sulphur, which may be re-obtained in a solid state by the method of testing above described.

In discussing the nature of flame, and the causes of its luminosity and heat, allusion has been made to the high temperature of that of hydrogen. This gas is occasionally employed for exciting intense heat; and, when mixed with oxygen, and burned as the mixture issues from a small jet, it produces a temperature nearly equal to that of the arc of flame in the voltaic circuit. A blow-pipe upon this construction was first made by Newman, and afterwards improved as to its safety, by Professor Cumming, of Cambridge. (*Journal of Science and the Arts*, 1, 67, and 2, 380.) Hemming's safety-tube has also been used in these experiments. (See *Phil. Mag.*, 3d Series, 1, 82.) An excellent mode of obtaining intense heat by the combustion of oxygen and hydrogen, consists in propelling the two gases, in their proper proportions to form water, from separate air-holders through a burner composed of two concentric tubes: a good form of such a burner has been described by Daniell. (*Phil. Mag.*, 3d Series, 2, 57.) The apparatus for this purpose has been further improved by Maugham, especially as relates to its application to the solar microscope. (*Trans. Soc. Arts*, &c. vol. 50.) The gases are now forced into a small chamber, terminated by a platinum jet, from which they are burnt. The heat is such that it is capable of fusing and even volatilizing platinum; it causes the melting of rock crystal, as well as alumina or clay. In this and similar cases where the inflammable gas is mixed with oxygen, the nature of the flame is materially altered, the combustion being entire throughout the body of the flame, and not limited to the film in contact with air. Hence, under these circumstances, the quantity of the combustible consumed, and the quantity of oxygen combining with it in a given time, are greatly increased. Owing to this perfect mixture of oxygen and hydrogen, the flame may be described as *solid*, possessing an intensely heating and penetrating power. Although scarcely visible in itself, the flame, when received on lime, asbestos, or platinum, emits an intense light (*see* page 92).

Lime was first used by Lieutenant Drummond as a source of light, with the oxyhydrogen jet, in 1826. (*Phil. Trans.* 1826, p. 324.) By means of it, in the Triangulation survey, he successfully connected the opposite shores of England and Ireland at or about Holyhead, a distance of sixty-four miles. In Scotland, he obtained a successful result on the summits of Ben Lomond and Knock Layd, a distance of ninety-five miles. (*Gas-Lighting Journal*, Jan. 1860.) Dr. Miller states that the *Drummond Light* has been seen at a distance in a right line of 112 miles. Coal-gas, and other inflammable gases and vapors, when mixed with oxygen in their combining proportions, burn, for the same reason, with what may be described as *solid* flames. As coal-gas, by being overheated in its manufacture, is converted in great part into hydrogen, it is not only substituted for this gas in aërostation, but also in producing the lime-light; so that, except for purely scientific purposes, the oxyhydrogen flame need not be employed as a source of light.

Compounds.—The range of combination of hydrogen is not so extensive as that of oxygen. It forms with metallic and non-metallic bodies the class of *Hydrides*. The hydrides of the metals are few in number, those of arsenic and antimony being the principal. There are three other metals which form temporary combinations with hydrogen—namely, potassium, tellurium, and zinc. Among non-metallic bodies it forms an alkali with nitrogen; neutral compounds with carbon and phosphorus; and acids (the class of *hydracids*) with chlorine, bromine, iodine, sulphur, selenium, fluorine, and cyanogen. These compounds are, for the most part, products of art. At a red heat, hydrogen is a powerful reducing agent; thus it readily decomposes the oxides, chlorides, and sulphides of some of the metals, combining with the oxygen, chlorine, or sulphur, and setting free the metal in a pure and finely-divided state. A current of dry hydrogen passed over oxide of copper, or oxide of iron, heated to redness in a tube, takes the oxygen to form water, which may be collected in a condensing bulb, or tube. The quantity of oxygen contained in the dry oxides may be thus determined.

Equivalent.—The equivalent, or combining weight, of hydrogen, is, by most English chemists, taken as unity—1: it is the standard with which the atomic weights of all other bodies are compared. Its volume equivalent in gaseous combinations is double that of oxygen, and has been variously assigned as two volumes or one. We can perceive no sufficient reason for departing from the simplicity of the rule hitherto received, that hydrogen shall be regarded as representing unity by volume as well as by weight. To assume that there are two standards, and that hydrogen represents weight, while oxygen represents volume, presents no advantages in the construction of chemical formulæ, or in the explanation of chemical facts.

Tests.—Special Characters.—As a gas, hydrogen is easily identified: 1. by its inflammability, and the production of water as a result of its combustion: 2. by its lightness: 3. by its insolubility in water, in solution of potassa, and in all liquids: 4. when free from oxygen, by its giving no red vapors when mixed with deutoxide of nitrogen; and by the mixture, in equal parts, burning without explosion, with a greenish-white flame: 5. by its being entirely converted into water when mixed with half its volume of pure oxygen, and the gases are combined by the electric spark, by heat, or by the action of spongy platinum. For the detection of hydrogen, when in intimate combination with carbon and oxygen in organic compounds, another process must be resorted to. Hydrogen, it is well known, at a red heat, decomposes oxide of copper, and is converted into water (*see* p. 117). The organic substance (starch) is first deprived of water by complete desiccation. It is then mixed with dry oxide of copper, placed in a tube, and heated to redness. The water produced is collected by passing the products through a balanced tube containing chloride of calcium. The increase of weight in the chloride represents the total amount of water formed; and one-ninth part of this, represents the amount of hydrogen contained in the substance under examination. The process for detecting and separating hydrogen is included in that which is employed for the determination of water.

Nascent or Allotropic Hydrogen.—Although the existence of two forms of hydrogen is unknown, yet as it is evolved from water by electrolysis, or as it is produced in the nascent state by chemical changes, the gas appears to have much greater energy in combining, than that which has been once set free. It has been long known to chemists, that, under these circumstances, gases frequently display great chemical power. In 1841, Mr. Smee noticed that porous coke or charcoal, which had formed either the negative pole of a battery, retained a portion of hydrogen, and when placed in a solution of sulphate of copper, the coke or charcoal was covered with the reduced metal. Free hydrogen has no power of decomposing a salt of copper, but in this state it was replaced by the metal. (*Elements of Electro-Metallurgy*, 1841, p. 37.) Ozann and Fremy have made similar observations regarding silver. If hydrogen is received on platinum sponge from the negative electrode of a battery, until bubbles of the gas begin to appear, it will be absorbed and condensed by this porous body. When the platinum sponge was washed and placed in a solution of sulphate of silver, there was immediately a precipitation of metallic silver. It was also found, that if the hydrogen evolved from the negative platinum electrode in the decomposition of water, was conveyed immediately into a solution of sulphate of silver, the metal was precipitated. When the gas was conducted into water containing perchloride of iron, with a trace of ferricyanide of potassium, Prussian blue was formed. These results could not be obtained with hydrogen gas in its ordinary state. When a current of hydrogen is passed into water containing ammonio-chloride of platinum diffused through it, there is no change. If the hydrogen is generated by zinc and sulphuric acid in the midst of the ammonio-chloride, there is an immediate decomposition, and finely divided platinum (platinum black) is set free.

If some granulated zinc is placed in diluted sulphate of indigo, and sulphuric acid is added in sufficient quantity to generate hydrogen in small bubbles, the indigo is slowly bleached. If the bleached liquid is exposed to the air, it will reacquire its blue color. If zinc is placed in a mixture of diluted sulphuric and nitric acids, few or no bubbles of gas escape; but ammonia is produced by the hydrogen, in the nascent state, entering into combination with the nitrogen of the nitric acid. The liquid after some hours will contain nitrate and sulphate of ammonia. In the rusting of iron in a damp atmosphere, in the oxidation of tin by nitric acid, in the effect of heat and of putrefactive changes on nitrogenous matter, ammonia is produced by nascent hydrogen combining with nitrogen, although hydrogen, when once free as a gas, shows no tendency whatever to combine with nitrogen.

These results, if they do not indicate an allotropic state of hydrogen, demonstrate that the combining properties of this element are widely different in intensity, according to the circumstances under which the observations are made.

In the electrolytic experiments above described, it has been proved that hydrogen may displace copper, silver, and other metals. Hence it has been supposed, that it is itself the vapor of a metallic body. Carbon and phosphorus might, however, with equal propriety, be ranked among metals.

CHAPTER X.

WATER ($HO=9$).—AQUEOUS VAPOR.—ICE.

History.—Water is an important constituent of the globe. As a liquid it covers three-fourths of the earth's surface, forming the ocean. In the atmosphere it is universally diffused as an invisible vapor, sometimes precipitated in the solid state as hail or snow, at others assuming the form of clouds or rain. The surface of the earth is itself covered with large masses of water, disposed in lakes and rivers. There is scarcely a rock or soil into which water does not penetrate. All the superficial strata contain it, and it is found in a great number of minerals, in a proportion varying from two to twelve per cent. of their weight. It exists in the three states in which matter is known to us: 1, as vapor or gas; 2, as a liquid; 3, as a solid. The range of water as a *liquid*, is well known to be between 32° and 212°. It is so abundantly found that there is no need to prepare it artificially; and it is easily separated from the foreign ingredients with which it is naturally associated, by converting it into vapor and subsequently condensing this vapor.

Water was long regarded as an element, and was supposed to be convertible into earth, until Lavoisier, in 1773, showed the fallacy of this notion. Cavendish and Watt, in 1781, demonstrated the production of water by the combustion of oxygen and hydrogen; and the former, to whom the important discovery of its composition is strictly due, proved the correspondence in weight of the resulting product with that of the gases used in its formation. Lavoisier first resolved water into its constituents, and Humboldt and Gay-Lussac proved that the volume of the oxygen to the hydrogen was exactly as 1 : 2. The relative weights of these gases were carefully determined by Berzelius and Dulong, and shown to be very nearly as 88·9 : 11·1, or 8 to 1.

Chemical Composition.—Viewed in a chemical aspect, water is a perfectly neutral oxide of hydrogen. The two gases combine in certain proportions by weight and volume, but only under fixed conditions. If placed in contact, they simply mix or diffuse with each other. When, however, two volumes of pure hydrogen are mixed with one volume of pure oxygen, and the mixture is inflamed in a proper apparatus by the electric spark, they totally disappear, and water in equal weight to the gases consumed, is formed. Again, if water is exposed to electrolytic action, it is resolved into two volumes of hydrogen, disengaged at the negative pole or cathode, and one volume of oxygen, disengaged at the positive pole or anode; so that water is thus proved by *synthesis*, and by *analysis*, to consist of two volumes of hydrogen combined with one volume of oxygen. The specific gravity of hydrogen, compared with oxygen, is as 1 to 16; these numbers, therefore, represent the comparative weights of equal volumes of those gases; but as water consists of one volume of hydrogen and half a volume of oxygen, it is obvious that the relative weights of these elements in that compound will be as 1 : 8. The accuracy of these numbers has been determined by the elaborate investigations of Dumas, (*Recherches sur la Composition de l'Eau, Ann. Ch. et Ph.*, Juin, 1843,) Regnault, and other chemists.

	Atoms.	Weights.	Per Cent.	Volumes.
Hydrogen	1	1	11·09	1·0
Oxygen	1	8	88·91	0·5
Water	1	9	100·00	1·

These results nearly correspond to the weights of the two elements, as deduced from their specific gravities. Thus, taking the specific gravity of hydrogen at 0·0691, and of oxygen at 1·1057, then 0·0691 × 2 = 0·1382 + 1·1057 (sp. gr. of O) = 1·2439; and 1·2439 : 1·1057 : : 100 : 88·89. The specific gravities of the constituents thus give for the composition of water 88·89 of oxygen, and 11·11 of hydrogen. The specific gravity of aqueous vapor, compared with air as 1, is found to be 0·622. This corresponds to one volume of hydrogen and half a volume of oxygen in each volume of vapor:—

1 volume of hydrogen	sp. gr.	= 0·0691
½ volume of oxygen	"	= 0·5528
1 volume of aqueous vapor	"	= 0·6219

The volume of aqueous vapor formed is always equal to the volume of hydrogen consumed. At mean pressure, and at the temperature of 212°, the volume of this vapor is 1689 times that of the water which produces it; in other words, a cubic inch, or rather more than half an ounce of water will be converted at 212°, into 1689 cubic inches, or about six gallons of vapor. 100 cubic inches of the vapor weigh, at the temperature of 212°, and under mean pressure, 14·96 grains, and at 60°, 19·34 grains.

The experiments illustrating the composition of water and showing the proportions in which its elements are united, may be arranged under *synthesis* and *analysis*.

Synthesis.—If a current of hydrogen is burnt under a funnel-tube connected with a condenser, the gas unites to the oxygen of the air, producing aqueous vapor, which may be collected in a receiver. The water thus condensed frequently has a slightly acid reaction, apparently from the simultaneous combustion or oxidation of a portion of the nitrogen of the atmosphere, so that nitric acid is produced. According to Saussure, if the hydrogen is in excess, the water may contain ammonia. (*Ann. de Chim.*, vol. 71, p. 282.) This experiment may be modified by burning a small jet of hydrogen under a tall and capacious bell-glass (provided with a stopper), supplying below, by another jet connected with a gas-holder, a stream of oxygen equivalent to half the volume of hydrogen. The bell-glass may be placed in a glass dish, and the jets may be passed through a perforated cork placed in the centre of the opening of the bell-glass, and so arranged that they are nearly in contact. The water produced, as a result of combustion, will trickle down the sides of the vessel, and may be collected in the dish.

One of the best synthetical processes for the production of water, however, is that which was employed by Dumas in his experiments on its composition. It consists in reducing a known weight of dry oxide of copper by pure and dry hydrogen. The current of hydrogen is purified and dried by the methods already described. (Page 108.) The oxide is placed in a bulb of hard glass, which can be maintained at a red heat without fusing, and which is exhausted of its air before commencing the operation. This is connected with another glass bulb, kept cool in order to condense and collect the water produced. When the oxide of copper is heated to full redness, and hydrogen is passed over it, only so much oxygen is taken by the hydrogen, as will suffice to form water. Hence the loss of weight in the oxide after the experiment, represents the oxygen consumed, and by deducting this from the weight of water condensed, the amount of hydrogen combined with the oxygen may be readily found. By this arrangement, Dumas produced in one operation, upwards of two ounces of water. The results which he obtained, correspond as nearly as possible to those already given—namely, in 100 parts by weight—88·888 oxygen, and 11·112 of hydrogen.

If two measures of pure hydrogen are mixed with one of pure oxygen, and the mixture is detonated by an electric spark, in a graduated glass tube, standing over mercury, the gases will disappear. If there be any excess of either gas, the portion in excess will remain unconsumed. At the moment the explosion takes place, the gaseous mixture becomes greatly expanded, probably to fifteen times its original bulk (Davy *on Flame*, p. 90), and a portion is apt to escape at the bottom of the tube; hence to prevent any loss, the experiment should be performed over mercury in a syphon tube.

Oxygen and hydrogen have no tendency to combine when mixed as gases, but when they are suddenly submitted to violent mechanical compression, the heat of condensation causes them to unite with combustion, and water is produced. (Biot.) A red heat, visible by daylight, inflames the mixture; but a dull red heat only causes the slow combination of the gases without explosion. Graham states that if a mixture of oxygen and hydrogen be heated in a vessel containing a quantity of pulverized glass, or any sharp powder, they begin to unite, in contact with the foreign body, in a gradual manner without explosion, at a temperature not exceeding 660°.

In the year 1824, Döbereiner found that spongy platinum, procured by heating the dry ammonio-chloride, on platinum foil, possessed the singular property of causing the immediate combination of hydrogen and oxygen, with heat sufficient to render the metal red hot, and to inflame the gases. If freshly prepared spongy platinum be held on filtering paper, over a jet of hydrogen issuing from a small tube into the atmosphere, it will soon become hot enough to inflame the gas. If a mixture of oxygen and hydrogen, or of atmospheric air and hydrogen, not in explosive proportions, be submitted to the action of the platinum, the gases enter into slow combination, water is gradually formed, and if there is a sufficiency of oxygen, the whole of the hydrogen will disappear under its influence; if, on the other hand, there is an excess of hydrogen, the oxygen will disappear, and the surplus hydrogen remain. In the analyses of the atmosphere and certain gaseous mixtures, platinum, in this peculiar state of mechanical division, becomes a valuable agent. For its more convenient application to such purposes, and to prevent the danger of explosion, the platinum is mixed with an equal weight of pure clay, and moulded with a little water into small balls, which, after having been slowly dried, should be gradually heated to a high temperature in a Bunsen's jet. For the purpose of manipulation, a small piece of platinum wire may be fixed in the balls while moist. These balls may be conveniently introduced into gases standing over dry mercury; their power is not impaired by use, for they may always be rendered efficient, or their power restored, by again heating them red hot. The admixture with clay not only gives cohesion to the platinum, but prevents the rapid heating of the metal, and therefore the explosion of the gases. This will be found a convenient method of analysis. If the gases are pure, and in their proper portions, the whole will disappear, and the mercury will rise and fill the tube. If there should be a residue, the amount of oxygen and hydrogen which have combined to form water, may be easily determined. Two-thirds of the condensed gases will represent the hydrogen, and one-third the oxygen.

Spongy platinum effects the union of oxygen with several other gases, such as with carbonic oxide, and, at high temperatures, with olefiant gas; it also causes the decomposition of deutoxide of nitrogen by hydrogen, producing ammonia. (Dulong and Thenard, *Ann. de Ch. et Ph.*, 23, 440.) It is an essential condition in all cases of the catalytic influence of platinum, that its surface should be absolutely clean, the slightest film of foreign matter—a result of mere exposure to air—impairing, or in some instances preventing the action: hence the advantage derived from carefully heating spongy platinum, which has become inert, in a clear flame. Some other metals, such as palladium and iridium, operate in the same manner, but less perfectly than platinum. Spongy platinum placed in hydrogen or in oxygen gas, separately, has no influence on the gases, and undergoes no change. It is in the state of mixture, or when one gas can come freely in contact with the other, that any effect is produced. If freshly-prepared spongy platinum is placed on mica, on a stand so arranged that the open mouth of a jar of hydrogen can be suddenly lowered over it, the platinum retains its usual appearance, and the hydrogen is not absorbed. If, however, the jar is raised so that the mouth is on a level with the platinum, the metal will become red hot, and the hydrogen will disappear, owing to its admixture with the oxygen of the air at this point. The heat is sometimes sufficient to kindle the hydrogen with a slight explosion. If this experiment is performed on the mixed gases, they should be in small quantity, and contained in a stout glass jar, as the explosion is sudden and violent. Spongy platinum placed on mica, or platinum foil or gauze, undergoes no change in air, but if a jet of dry hydrogen be allowed to fall on it from a bladder, it will become red hot and ignite the gas. In all cases the platinum acts most efficiently when freshly prepared, or when it has been heated before the performance of the experiment.

Faraday has found that perfectly clean platinum *foil* or *wire* will also cause the combination of oxygen and hydrogen. He refers this phenomenon to a peculiar attraction between the clean metallic surface and the particles of the gaseous mixture, resembling that by which bodies become wetted by fluids with which they do not combine chemically, or in which they do not dissolve; or the attraction which renders certain bodies hygrometric, although they neither dissolve in, nor combine with water. By this surface-attraction, the particles of oxygen and hydrogen are so approximated and condensed, as to enter into chemical union; and, in so doing, to evolve sufficient heat to raise the temperature of the metal. It is calculated that platinum in the state of sponge, will absorb 253 times its volume of the mixed gases, and condense them to 1-1000th of their bulk.

Analysis.—Water may be decomposed, or resolved into its elements, by a variety of processes. One of these, based on the decomposition of aqueous vapor, by passing it over iron wire heated to redness in a tube, has already been referred to, as a source of hydrogen (*see* page 108). In a carefully conducted experiment, the iron will be found to have increased in weight; and this increase, added to the weight of the hydrogen collected, will be equal to the weight of the water which has disappeared.

Electrolysis furnishes the best method of analyzing water, in order to determine its chemical constitution, as well as the volumetric proportions of its constituent gases. By a simple apparatus, oxygen and hydrogen are separately collected, and it may be observed, during the action of the battery, that for every cubic inch of oxygen given off at the positive electrode, there are two cubic inches of hydrogen collected at the negative electrode. These gases when mixed over mercury may be recombined in the manner already described (page 117). They entirely disappear, and are reconverted into water. Analytically and synthetically, therefore, the constitution of water has been accurately determined. Pure water is not easily decomposed by electrolysis; but its decomposition is readily brought about by the addition of a tenth part of sulphuric acid. The oxygen evolved possesses some peculiar properties (*see* 101).

Varieties of Water.—Water in its ordinary state, such as spring and river water, is always so contaminated with foreign substances as to render it unfit for chemical purposes. *Rain-water* is more pure, but it frequently contains small quantities of sulphuric, nitric, and hydrochloric acids, in combination with ammonia, lime, or other bases, as well as organic matter of animal or vegetable origin. Rain-water collected near the sea, invariably shows traces of chlorides; its impurities vary much with locality. In Paris, it has been found to contain traces of iodine and phosphoric acid. Even if collected in clean glass vessels, before it has touched any roof or soil, it is always found impure in or near inhabited places.

Lake-water.—Among the purest forms of natural water may be mentioned lake-water, as it is collected in deep lakes and in slaty and granitic districts. Among pure waters of this kind in Great Britain, is that of Loch Katrine, in Scotland, containing only two grains of solid matter in the imperial gallon. The waters of Loch Ness, and of Enerdale Lake in Cumberland, are nearly equally pure.

River-water is subject to great variation in quality, according to the nature of the soil, and other accidental circumstances. It may be regarded as rain-water holding dissolved, substances derived from the atmosphere and the soil over which it has flowed. It is this kind of water which is now largely employed for the supply of towns. The properties of good River-water are —(1) It should be colorless, tasteless, and free from smell. (2) It generally has an alkaline reaction from the presence of carbonate of lime, held dissolved by carbonic acid. This is the principal mineral constituent of river-water in the southern and eastern districts of England. (3) It gives a slight white precipitate when nitrate of silver is added to it; this precipitate is not entirely dissolved by nitric acid (chloride of sodium). (4) It gives a primrose-yellow colored precipitate, with a solution of arsenio-nitrate of silver. This indicates the predominance of an alkaline carbonate, generally bicarbonate of lime. The presence of bicarbonate of lime is also known by an alcoholic solution of logwood striking a violet color with the water. As the bicarbonates of potassa and soda also produce this change of color, a solution of chloride of calcium should be added. Bicarbonate of lime is not precipitated by this salt. (5) It gives, after a time, only a slight white precipitate, when a solution of nitrate of baryta is added; this precipitate being insoluble in nitric acid (sulphuric acid). (6) A white precipitate when treated with oxalate of ammonia, more abundant than with any of the other tests (lime). (7) When boiled, it does not become milky-looking or turbid, or it presents this appearance only in a slight degree (precipitation of carbonate of lime). (8) When a standard diluted solution of permanganate of potassa is added to a few ounces, the color is not discharged at a temperature below 160° (absence of organic matter.)

In respect to the last character, it may be observed, that if the color is discharged, it indicates, in the absence of foul effluvia, the presence of organic matter; and the greater the amount of permanganate decolorized before the water retains a pink color, the larger the quantity of organic matter present. If a graduated tube or burette is employed, two waters may thus be compared, in reference to the quantity of organic matter contained in them, or they may both be compared with an artificial standard. At common temperatures, the organic matter acts very slowly on the permanganate. At a high temperature, the permanganate itself is decomposed, although no organic matter is present. M. Monnier found that this change took place at 194° F., and that if the water were not heated above 160°, a safe inference might be drawn from the results.

These are the principal chemical reactions of river-water. They show the presence of chlorine, carbonic acid, sulphuric acid, and lime, and generally indicate the existence of common salt, bicarbonate and sulphate of lime, as well as of organic matter. Salts of magnesia and potassa, with alkaline nitrates, oxide of iron, silica, and phosphoric acid are frequently contained in river-water, in smaller proportion; and they may be easily detected by other processes applied to the residue left by the water after evaporation.

Among other properties, it may be observed, that river-water does not readily dissolve soap. If a solution of soap in alcohol be added to some ounces of the water, and the mixture is well agitated, a white curdy substance is formed (a compound of the fatty acids of soap with the calcareous and other bases of the water), and the water is rendered milky-looking; but there is no persistent frothiness as with pure water. On this property is founded the process of determining the *hardness* or *softness* of water, by means of the soap-test. The method of employing this will be presently explained. The larger the quantity of calcareous and magnesian salts, the harder the water; while the more free the water is from any saline matter, the softer it is. River-water, as it is ordinarily constituted, has so little action on the metal *lead*, that even after keeping the water in a leaden vessel for a considerable time, it will either show no trace of lead, or the quantity is so small, that it may be disregarded. The waters of English rivers, however, vary so much in this respect, that each water should be submitted to a separate trial, whatever may be its chemical composition. Thus, river-waters which contain soluble nitrates, or chlorides in unusual quantity, generally act upon lead. This chemical effect depends not merely on the nature of the salts, but on the proportion in which they are contained in the water.

The solid residue left by the evaporation of river-water varies in weight from 6 to 50 grains, or more, in the Imperial gallon; but potable river-waters are generally comprehended between these two extremes. The nearer the point from which the water is taken to the source of a river, the more free from saline and other impurities will it be found. The Thames water formerly supplied to London, yielded from 20 to 24 grains of solid residue, from the Imperial gallon of 70,000 grains. That which is now supplied from the river, taken near Hampton, yields only from 15 to 17 grains in the gallon, varying a little with the season of the year, and the amount of rain. All foreign substances in water have been described as "impurity." In a chemical sense this is correct, but the presence of carbonate of lime (chalk) and chloride of sodium (common salt), in river-water, in the small proportions in which these substances are found therein, is not injurious to health. The salubrity of districts bears no relation to the greater or smaller quantity of saline matter in water. If distilled water could be supplied to a population in millions of gallons daily, it would be neither agreeable nor wholesome to the general public. The experiments of M. Boussingault have clearly proved that the calcareous salts of potable waters, in conjunction with those contained in food, aid in the development of the bony skeletons of animals. (*Pelouze and Fremy*, *Traité de Chimie*. 1860. Vol. i. p. 234.) Calcareous waters, such as Carrara water, are usefully employed in medicine. The search after non-calcareous water therefore is based on a fallacy. If lime were not freely taken in our daily food, either in solids or liquids, the bones would be destitute of the proper amount of mineral matter for their normal development.

With respect to the chloride of sodium, which has been wrongly described as a result of the presence of sewage in river water, it may be safely said that no natural water taken from the purest sources in the world, has been yet found without it. All river and spring waters contain it in greater or less proportion.

The solid contents in the imperial gallon of some principal river waters of Europe have been found to be as follows: The Thames at Greenwich, 27·79 grains, at Hampton 15 grains; the Seine in Paris, 20 grains; the Rhone at Lyons, 12·88 grains (Bineau); the Rhine at Basle, 11·97 grains (Pagenst); the Garonne at Toulouse, 9·56 grains (Deville); the Loire at Mehung, 9.42 grains; the Scheldt in Belgium, 20·58 grains; and the Danube, Vienna, 10·15 grains (Hauer). The principal salts in these waters are the carbonate and sulphate of lime, with chloride of sodium.

In conducting an *analysis* of a potable water, the general course to be pursued is the following: 1. To determine the solid contents by the slow evaporation of a gallon, or at least half a gallon of the water, filtered or unfiltered, according to circumstances. In good river water the residue thus obtained is white, or of a pale fawn tint; and it will weigh, when dry, from 6 to 20 grains. 2. The organic or combustible matter is next ascertained by heating the dry residue to a low red heat, and noting the loss of weight. 3. To determine, by the usual modes of analysis, the nature and proportion of the salts contained in this residue. 4. To ascertain whether the water has any action on lead. A clean bar of this metal, exposing an area of from 8 to 12 square inches, should be immersed in the water and the vessel freely exposed to air. In 48 hours the water may present a milkiness or remain clear. In either case it should be tested for lead by passing into it a current of washed sulphuretted hydrogen gas. 5. To determine the relative hardness of the water. A saturated solution of Spanish soap is made in three parts of rectified spirit (0·830) and one part of distilled water. After sufficient digestion the solution is filtered, and it then serves as a soap-test. The solution is added from a graduated vessel to from four to eight ounces of distilled water contained in a bottle; and the quantity required to produce a permanent froth in the water is noted. This forms a standard for comparison. A similar quantity of river water is treated in another bottle with the same solution of soap; and it will be found to require five, six, ten, or twelve times the quantity of soap-solution to produce an equal amount of permanent froth in it, as in the distilled water. The river water may thus be described as having 5°, 6°, 10°, or 12°, of hardness, *i. e.*, it will require these additional proportions of soap to produce in it the same detergent properties, as in a like quantity of distilled water. Dr. Clark's soap-test is based on a different principle. He makes an artificial solution of chloride of calcium, and uses a weak alcoholic solution of white curd-soap. His degrees, therefore, are referable to a different standard.

Spring Water.—Spring waters may be divided into those which are derived from shallow wells, and those which issue from deep springs, called also *Artesian* wells. The former are generally within thirty to fifty feet of the surface, while the latter in the London district are from 400 to 600 feet in depth, and in Paris they reach a depth of 1800 feet. The water from the shallow wells of London usually abounds in sulphate and carbonate of lime, containing generally but little chloride of sodium; the solid contents of the gallon are very variable, but sometimes amount to 130 or 140 grains. The water is very hard, and yields in some cases traces of sewage, gas-liquids, or the products of their decomposition. The deep (Artesian) wells which penetrate the London clay, and are carried to different depths into the underlying chalk, vary in the quality of their water according to the care with which the superincumbent springs have been excluded: they contain a larger relative proportion of solid matter than river water, but less than that found in the surface-wells, and are remarkably characterized by the abundance of soda-salts and by their alkalinity, which is derived from bicarbonate of soda: like all other spring waters, they hold more or less carbonic acid. They generally contain from 50 to 70 grains of saline matter in the imperial gallon. The water of the Trafalgar-square springs, issuing from a depth of 510 feet, contains 68·94 grains of saline matter in the imperial gallon, including 14 grains of carbonate of soda, 19 grains of sulphate, and 25 grains of chloride of sodium. The well at the Royal Mint has a total depth of 426 feet. It contains less than 38 grains of solid matter in the gallon: including 8·63 grains of carbonate of soda, 13·14 grains of sulphate of soda, and 10·53 of chloride of sodium. The water of the well at Southampton, issuing from a depth of 1360 feet, contains 68 grains of saline matter in the gallon, of which 18 grains consist of carbonate of soda, 8 grains of sulphate, and 20 grains of chloride of sodium. The Artesian well-water of the Paris Basin (Grenelle), issuing from a depth of 1794 feet, is much purer than the London Artesian waters. It contains 20 grains of saline matter in the gallon, of which nine grains are carbonate of lime, and four grains are bicarbonate of potassa—the principal saline ingredients. The Artesian well-waters differ from those of surface wells in containing generally a larger quantity of phosphates and a smaller proportion of calcareous salts and of organic matter.

Distilled Water.—When spring or river water is distilled, the solid contents are left in the retort or still. In the chalk district this residue consists in great part of carbonate of lime, with some sulphate of lime, of carbonate and sulphate of soda, with magnesia, silica, alumina, and oxide of iron. In ordinary waters, besides carbonate and sulphate of lime, the insoluble matter deposited has been found to contain traces of lead, copper, arsenic, and other metals. The condensed water obtained in the receiver, as it is commonly distilled, always contains foreign matter. The first portions are frequently impregnated with ammonia; these should be rejected, and, when four-fifths have been distilled, the operation should be stopped. Water distilled in glass is sometimes alkaline, owing to its dissolving a portion of soda from the glass. It can be considered perfectly pure only when it has been redistilled at a low temperature in silver or platinum vessels.

Pure water is transparent, and without either color, taste, or smell. It should be quite neutral. Its neutrality may be tested by adding at least a pint of it to a small quantity of a strong solution of litmus, reddened to a port wine tint by tartaric acid. If the water is neutral the addition of it to this solution of litmus, will not render the liquid blue or more strongly redden it. Its chemical properties are chiefly negative. It should give no precipitate with nitrate of silver, nitrate of baryta, oxalate of ammonia, or ammonia. It should undergo no change of color on passing into it a current of sulphuretted hydrogen gas. On adding to some ounces of the water a few drops of a solution of ammonio-nitrate of silver and exposing the vessel containing the water to solar light, it should undergo no discoloration. The pink color imparted to the water by a weak solution of permanganate of potassa should remain unchanged. These last mentioned tests by their negative results, show the absence of organic matter and foul effluvia. Half a gallon of the water should leave no ponderable residue on evaporation. Acetate of lead frequently produces in distilled water a white precipitate owing to the presence of carbonic acid. The precipitate is soluble in acetic acid. If a brown precipitate is produced by this test, it indicates the presence of sulphuretted hydrogen. Among other properties, a solution of soap in alcohol produces no curdiness or opacity in pure water, but the soap is readily dissolved; on agitation the water remains clear, and presents a persistent frothy stratum on its surface. If a piece of clean sheet lead be immersed in pure distilled water, the water rapidly becomes opaque, from the production of hydro-carbonate of lead. Distilled water, free from impurity, is indispensable to the chemist. The water obtained by melting pure ice may be occasionally substituted for it.

In reference to *physical* properties, pure water is a powerful refractor of light, but it is a very imperfect conductor of *heat* and *electricity*. In reference to the latter force, pure water so completely resists the passage of a current, that it has been even doubted whether it was an electrolyte. This resistance becomes, therefore, a test of the purity of water. The electrolysis of common water probably depends on the saline matter which it holds in solution. In such experiments on distilled water, it is necessary to add to it a small quantity of sulphuric acid. The following experiments will prove that it is a very imperfect conductor of *heat:* Fill a long test-tube with distilled water, and freeze the lower three inches by immersing the end of the tube in a mixture of ice and salt. When the lower part has been thus frozen, the upper stratum of water may be boiled over a spirit lamp and kept boiling for a considerable time without melting the ice below. Lay a thermometer on the bottom of a shallow porcelain dish; cover it with a thin layer of water—pour on this a stratum of ether and ignite it. When the ether is consumed, although the surface of the water was heated far beyond its boiling point, it will be observed that the thermometer has scarcely been affected. The sides of the vessels used in these experiments may, however, conduct heat downwards. The experiment may be varied by placing in a jar of water an air-thermometer, containing colored fluid with the bulb upwards and nearly touching the surface of the water. Float upon the water a small copper basin containing ether; this may be inflamed, and during its combustion, although the surface of the water is heated to a high temperature, the air-thermometer will be but slightly affected. Fill a test-glass to two-thirds of its capacity with water, and place in this a mercurial thermometer, the bulb resting on the bottom of the glass. Now pour carefully upon the cold water some boiling distilled water which has been slightly tinted with blue litmus. The colored water will float on the cold water in the glass; but, although at 212°, the thermometer will indicate no change of temperature, except by the heat slowly transmitted downwards by the sides of the vessel. These facts clearly demonstrate that unlike solids this liquid cannot transmit heat from the surface downwards.

The only mode of distributing heat through water and other liquids is by a kind of diffusion, depending on a change of density. Hot water is lighter than cold, as one of the above-mentioned experiments proves. If, therefore, the bottom of a vessel containing water is heated, the liquid will rise as its specific gravity is diminished, and there will be a series of upward and downward currents until the water has acquired a uniform temperature. This may be shown by heating water in which are diffused particles of camphor, precipitated from its alcoholic solution. The motion of these or of any other light solid diffused through the liquid, will indicate the course of the currents.

Water is expanded by heat, but its rate of expansion is *cæteris paribus* less than that of other liquids, and the ratio of increase is augmented by the temperature.

Distilled water is assumed as a standard to which the relative weights of all solids and liquids may be compared—its *specific gravity* being called 1·000. (In reference to this subject, the reader will find in the *Appendix* a description of the methods by which the specific gravities of all solids and liquids, whether lighter or heavier than water, may be taken. The scale of Baumé, much used on the Continent, is also given in a comparative table.)

At the temperature of 62°, which is that to which specific gravities are usually referred, a cubic inch of water weighs 252·458 grains; or at 60°, the cubic inch weighs almost exactly 252·5 grains, and the cubic foot 998·217 ounces *avoirdupois*, which is so near 1000, that the specific gravity of any substance, in reference to water, is very near the absolute weight of one cubic foot of such substance in avoirdupois ounces. The specific gravity of gold, for instance, is 19·3, in reference to water as unity; and, therefore, a cubic foot of gold weighs nearly 19,300 ounces. Water is about 815 times heavier than atmospheric air. At mean temperature, it is assumed as the unit to which the specific heats of bodies, especially of solids and liquids, are usually referred.

The density of water varies with the temperature. It attains its maximum density at 39°·39, or about 40°; hence water expands from this point, whether the thermometer falls from 40° to 32°, or whether it rises from 40° to 48°. It is a remarkable confirmation of this fact, that the temperature of the deep sea in all latitudes has been found to fluctuate about 40°.

Water is said to be colorless, but when looked at in a large mass it has a greenish-blue color. This is well seen in the waters of Matlock and other springs, and in the glaciers of Switzerland. Most river waters have a slightly yellowish color from the presence of organic and ferruginous substances. A small quantity may show no color, but when a gallon is examined in a tall glass vessel, placed on a sheet of white paper, the color may be seen. The purest distilled water presents a color if examined in a column of sufficient length.

Water is susceptible of compression, as was originally shown by Canton. Perkins states that a pressure of 2000 atmospheres occasions a diminution of only 1-12th of its bulk. (*Phil. Trans.*, 1820.) According to the experiments of Oersted, and those of Colladon and Sturm (*Ann. Ch. et Ph.*, xxxvi. 140), its absolute diminution of bulk for each atmosphere is not more than the 51·000·000th of its volume. It is stated by Dessaignes, that when water is submitted to very sudden compression, it becomes luminous. (Thenard, *Traité de Chimie*, i. 432.)

Ice.—At the temperature of 32° water congeals into ice, which, if slowly formed, produces needles crossing each other at angles of 60° and 120°. The forms are various, but the primitive figure is that of a regular six-sided prism, belonging to the rhombohedral system. Although the freezing of water is commonly said to take place at 32°, yet if the water be in a glass tube, one-fourth of an inch in diameter, it may be cooled to 23° without freezing. When cooled to 21° it freezes at once. In a capillary tube of 1-200th of an inch diameter, Mr. Sorby found that water did not freeze at 3°; when, however, it was cooled to 1°·4, it passed to the state of ice. (*Phil. Mag.*, August, 1859, p. 107.)

The specific gravity of ice varies from 0·918 to 0·950, but the densest ice, obtained by freezing water deprived of air, is always considerably lighter than water. According to Brunner, the contraction of ice by diminution of temperature exceeds that of any other solid; its density at 32° being 0·918, at 18° it is 0·919, and at 0°, 0.920. (*Ann. Ch. et Ph.*, July, 1845.) Ice is a non-conductor, or nearly so, of electricity, and under favorable circumstances becomes electric by friction. (Faraday's *Exp. Researches*, 4th Series, § 381 and 419.) It is a very bad conductor of heat, but it transmits radiant heat with such facility that Faraday was able to ignite phosphorus by converging the solar rays through an ice-lens. In freezing, water expands, and with such force as to burst the thick and strong vessels in which it is confined. The rupture of iron and leaden pipes is a familiar instance of this power of expansion. The greatest difference observed between the bulk of water before and after congelation was found to be in the ratio of 174 : 184. Exposed to the air, ice loses considerably in weight by evaporation.

The manner in which water frees itself of impurities in the act of congelation, is very remarkable; by careful freezing, it may be entirely deprived, not only of common air, but of those gases for which it has a strong affinity, as well as of all saline matters. In the common mode of freezing water, the extricated air is entangled in the ice, and renders it more or less porous and translucent; but if means be taken to remove the air bubbles, by agitation or otherwise, the resulting ice is dense and perfectly pellucid, as we sometimes see in icicles, or, more remarkably, when a thin glass tube or flask, containing water, is immersed in a freezing mixture, and constantly agitated by means of a feather, so as to brush off the air and water from the layer of ice which forms upon the sides of the vessel. This ice is not only perfectly transparent and free from air-bubbles, but it is also freed from saline matters, which are therefore contained in excess in the unfrozen water. This will be found to be the case with common spring water, but a better illustration consists in thus freezing water colored by sulphate of indigo, when the ice will not only be quite colorless, but, when rinsed in a little distilled water so as to cleanse its surface from the adhering mother-liquor, it will not contain a trace of sulphuric acid. In the same way an aqueous solution of ammonia, when properly frozen, yields ice which is quite free from all trace of the alkali. The beautiful masses of perfectly transparent ice, imported for the use of the table from Norway and from North America (Wenham Lake ice), yield perfectly pure water; they are formed in deep lakes, as a result of slow and gradual cooling, ending in congelation. It has long been known that wine and other alcoholic liquors are strengthened by partial freezing, and that the ice which they deposit is little else than pure water, and that lemon-juice and vinegar may be similarly strengthened; but the fact of spring water thus losing the whole of its saline and aerial contents was first pointed out by Faraday, and in these cases the unfrozen portion is, of course, rendered relatively impure, so that water may be concentrated by freezing as it is by evaporation. In northern regions, salt is obtained from sea-water by simply allowing the water to freeze. The blocks of ice, which are nearly pure water, are removed, and the residuary liquid is a comparatively strong brine, from which salt may be obtained by evaporation.

When ice is formed at temperatures a few degrees below the freezing-point, it has a well-marked crystalline structure, as is seen in water frozen from a state of vapor, in flakes of snow, or hoar frost. But ice formed in water at 32° is a homogeneous mass, breaking with a vitreous fracture, and presenting no crystalline structure (Graham). The changes which it undergoes in the movement of glaciers, is a proof that it possesses some plasticity.

Ice-water procured from the melting of the ice of deep lakes is one of the purest forms of natural water. We have found in it only minute traces of alkaline chloride. *Snow-water* is less pure, the fine crystals of snow in their formation lock up many organic and mineral ingredients which were diffused through the atmosphere, especially when collected in the neighborhood of towns. It frequently contains so much organic matter as to show confervoid vegetation under exposure to light. The amount of air in snow is very great. We have found that sixty cubic inches of snow, well compressed, will produce only eight cubic inches of water. To this diffusion of air among its particles it owes its whiteness. The water derived from melted snow is generally too impure to be employed for any chemical purposes.

Steam. Aqueous Vapor.—Water gives off a vapor at all temperatures, even at 32°. In its ordinary state, if exposed to heat in open vessels, it boils, or is converted at 212° into steam, the barometer being at 30 inches; but the boiling point of water varies with the pressure, and is influenced by the air which the water contains, as well as by the vessel in which it is heated. When quite pure and deprived of air, water may be heated to about 240° before it reaches the boiling point; at this temperature, however, it is suddenly converted into vapor with explosive violence. If a piece of pure ice be heated in a vessel containing oil, the heat may be continued until the water from the ice has reached a temperature of 240°, when the whole is converted into vapor with explosion. The tranquil ebullition of ordinary water at 212° appears, therefore, to be mainly dependent on the presence of air.

Water generally escapes in vapor unmixed with the solids which may be dissolved, but during rapid boiling, some portion of the solids is carried over with the steam. Thus the vapor of a boiling saturated solution of carbonate of soda has been observed to tinge of a yellow color, lights burning in the same apartment. This is owing to the combustion of a portion of sodium from the soda-salt evolved in the aqueous vapor. Even the most fixed solids may thus escape with steam. Boracic acid is collected in the lagoons of Tuscany by condensing the aqueous vapor in which it is dissolved; this vapor, charged with the acid, is continually issuing from the soil. Even mercury, one of the heaviest metals known, may be carried over with the vapor of water at 212° (*Chem. News*, Aug. 24, 1861).

Steam, or aqueous vapor, may be exposed to a full red heat (1000°) by passing it through iron tubes heated to redness, without undergoing any decomposition. That which is now called superheated steam, we have observed to issue from a discharge pipe at a temperature of 460°. In this highly heated state, the steam is put to various industrial uses without any danger. The only gas which we have found associated with the steam at this high temperature, was nitrogen. The decomposition of water by iron at a red heat appears to be here arrested by the production of the magnetic oxide of iron, which lines the interior of the tubes, and prevents further chemical action. Aqueous vapor has been rendered incandescent by the heat of the electric spark from Ruhmkorff's coil, and a spectralytic examination of the light, has shown that in this state it always gives the bright lines due to hydrogen.

When water is placed, in small quantities at a time, in a platinum or other vessel, heated to full redness, it does not boil, and does not produce any visible vapor. The liquid assumes what is called the *spheroidal* state, and rolls about in a stratum which presents a convexity on all sides, and nowhere touches the containing vessel. At this temperature, there appears to be a repulsion between the water and the metal. The liquid has been found by Boutigny to be a few degrees below its boiling point; it gradually diminishes in volume, and at last it evaporates entirely, leaving only the solid matters which it may have contained. If while the water is in this spheroidal state, the source of heat is suddenly withdrawn, the metal becomes cooled, and at a certain point the water comes in contact with the heated surface, and a large portion of it is suddenly converted into steam. The spheroidal state is common to all liquids. It may be well shown in water by first warming the liquid before pouring it, gradually, on the red hot metallic surface.

Water may be entirely decomposed into its constituent gases at a full white heat. Mr. Grove has proved that if a platinum ball, heated to whiteness, is plunged into water beneath a tube filled with water, the mere contact of the white hot metal liberates oxygen and hydrogen, which may be collected and exploded in the tube. Heat, like electricity, has therefore not only a composing, but a decomposing effect, on the elements of water.

CHAPTER XI.

WATER—PHYSICAL AND CHEMICAL PROPERTIES—HYDRATION—MINERAL WATERS—PEROXIDE OF HYDROGEN.

Relations to Heat.—The relations of water to *heat* are in many respects remarkable. Its *specific heat*, or capacity for heat, is greater than that of all liquids and solids. By this term we are to understand the relative proportion of heat necessary to raise equal weights of different substances from some lower to some higher temperature, or more generally, the relative quantity of heat contained in equal weights of different substances at the same temperature. This difference was called by Dr. Black the *capacity* of bodies for heat. Equal quantities of the same fluid, at different temperatures, give the arithmetical mean on mixture. Equal measures, for instance, of water at 70°, and of water at 130°, will give the mean temperature of 100°; that is, the hot water loses 30°, and the cooler water gains 30°. But if equal measures of different fluids, as, for instance, water at 70°, and of mercury at 130°, be mixed, the resulting temperature will not be the mean, or 100°, but only 90°. Here, therefore, the mercury loses 40°, while the water only gains 20°, hence the inference that the quantity of heat required to raise a given measure of mercury 100°, will only raise the same measure of water 50°: that is (speaking here of equal bulks), the capacity of mercury for heat is only = half that of water. But the capacities of bodies for heat are most conveniently referred to equal *weights* rather than measures; and if we thus compare water with mercury, it will be found that a pound of water absorbs thirty times more heat than the same weight of mercury; viewed, therefore, in this way, the capacity of water for heat, is to that of mercury as 30 to 1, or as 1000 to 33, and we generally thus express the capacities of bodies for heat by a series of numbers, having reference to water as 1000, such numbers representing their *specific heats.*

The most accurate determination of specific heat appears to be derived from the process of cooling, the time required for this purpose being directly as the specific heats of the bodies, provided they are carefully placed under similar circumstances: contained, for instance, in a polished silver vessel, in a vacuum. The following capacities were thus determined by Dulong and Petit:—

	Sp. Heat.		Sp. Heat.
Water	1000	Zinc	93
Sulphur	188	Silver	56
Glass	117	Mercury	33
Iron	110	Platinum	31
Copper	95	Lead	29

In reference to liquids, water stands higher than all others:—

	Sp. Heat.			Sp. Heat.
Water	1000	Oil of Turpentine		462
Alcohol	620	Sulphuric Acid	(1·84)	350
Ether	520	Nitric Acid	(1·36)	630
Olive Oil	438	Hydrochloric Acid	(1·15)	600

Among liquids, mercury is most easily heated and cooled: hence it is well adapted for thermometrical uses; while water requires a long time to be brought to a high temperature, and, when once heated, is a long time in cooling. It is by this property that large masses of water exert an equalizing influence on atmospheric temperature.

When solid passes into liquid water—in other words, when ice melts, a large amount of heat is absorbed, or rendered *latent.* Ice and water therefore contain different quantities of heat, although each may be at the same temperature, namely 32°. This may be proved by a simple experiment. If equal weights of water at 32° and 172° respectively, are mixed, the temperature of the mixture will be the mean of the two—namely, 102°. But if ice at 32° be mixed with an equal weight of water at 172°, the temperature of the mixture, instead of 102°, will be only 32°. Thus, in the substitution of ice for ice-cold water, there is a loss of heat to the amount of 140°. This expresses the *latent heat* of water at 32°, compared with that of ice at the same temperature; and it follows, that in reconverting the water into ice, this amount of heat, which was latent in the water (*i.e.* not appreciable to the thermometer), must be again set free. Hence, during a thaw, the temperature of the air near the surface of the earth, is lowered; while, on the other hand, in the act of freezing, water gives out a large amount of heat, which renders the temperature of the air milder.

The production of *freezing mixtures* depends on these principles. Equal parts of snow or finely powdered ice and common salt, will lower the thermometer from 32° to 0°. Both solids tend to assume the liquid state; the brine which results from their union, remains liquid nearly to zero. Two parts of snow or ice and three parts of powdered crystals of chloride of calcium, produce a mixture which will lower the thermometer to —50°, and thus freeze mercury. Solid carbonic acid and ether are now employed to produce a maximum of cold (*see* Carbonic Acid). Whatever causes the rapid liquefaction of solidified water, produces great cold. Thus, when ice or snow is mixed in equal weights with diluted sulphuric and nitric acids, together or separately, cold is produced.

Water may be cooled below 32°, without consolidating into ice; but the temperature of water in which ice is melting is always 32°, and does not rise above that degree so long as any ice remains unmelted. This is the degree of cold which is really represented as 32° by our thermometers, and as zero on the scale of Reaumur and Centigrade. Again, when water passes into steam or aqueous vapor, a still larger amount of heat is absorbed or rendered latent, so that a small quantity of water in the form of steam is sufficient, by condensation, to heat a large quantity of cold water. If 100 gallons of water at 50° be mixed with 1 gallon at 212°, the temperature of the whole 101 gallons will be raised by only 1·5°. But, if a gallon of water be condensed from the state of *steam* into a vessel containing 100 gallons of water, the water will in that case be raised 11°. A gallon of water, therefore, condensed from steam, raises the temperature of 100 gallons of cold water 9·5° more than the addition of a gallon of boiling water; consequently, if the heat imparted to 100 gallons of water by 10 pounds of steam could be condensed in 1 gallon of water, it would raise it to 950°; and a gallon of water, converted into steam of ordinary density, contains as much heat as would bring five and a half gallons of ice-cold water to the boiling point. The quantity of ice, which is melted by steam of mean density, is seven and a half times the weight of the steam.

The latent heat of steam and other vapors has been examined by Dulong, and on his researches the following table is based:—

Water	955°·8	Ether	174°·6
Alcohol	374°·4	Oil of Turpentine . .	138°·6

Hence the vapor of water has a greater amount of latent heat, or a greater amount of heating power in undergoing condensation, than the vapors of other liquids.

It is a well known fact that the conversion of water into vapor at any temperature is attended with the production of cold. The instrument invented by Dr. Wollaston, under the name of *cryophorus* (κρύος, ice, φέρειν, to bear), is constructed on this principle: it establishes the fact that water may be solidified, as a result of the cold produced by its own vapor. The instrument consists of a tube, having a bulb at each extremity, one of which is half filled with water; the interior of the tube is perfectly deprived of air by boiling the water in one of the bulbs, until a jet of pure steam issues through a small opening left at the bottom of the other, which is then sealed by fusion in the flame of a lamp; the consequence is, that the water in the other bulb is greatly disposed to evaporate; but this evaporation can only proceed to a certain extent, because the pressure of vapor within the tube soon prevents its further progress. To get rid of this, to keep up the vacuum, and to occasion a constant demand upon the water for the fresh formation of vapor, the empty ball is plunged into a freezing mixture, which continually condenses the vapor within, and so accelerates the evaporation of the water in the other bulb as to cause it ultimately to freeze.

These peculiar conditions of water in reference to heat have a manifest tendency to maintain it in a liquid condition, the state in which it is indispensable for animal and vegetable existence.

Water, which has been exposed to the atmosphere, always contains a portion of air, a fact which may be proved by boiling it, or by exposing it under the exhausted receiver of an air-pump. To separate the air, the water must be continuously boiled *in vacuo*, for it is obstinately retained. (Donny, *Ann. Ch. et Ph.*, Fev. 1846.) It absorbs oxygen gas from atmospheric air in preference to nitrogen, and, when the air is expelled by boiling, the last portions contain more oxygen than those first given off. (Humboldt and Gay-Lussac, *Journal de Physique*, 1805.) The presence of air or oxygen in water is known by the addition of protoferrocyanide of iron (*see* page 90).

If the white compound be added to recently boiled water, the rapid absorption of oxygen will be indicated by its acquiring a blue color.'

Dalton states, that 100 cubic inches of spring water yield about two inches of air, which, after losing from 5 to 10 per cent. of carbonic acid by the action of lime-water, consists of 38 per cent. oxygen, and 62 nitrogen. (*New System*, 271.) Dr. Henry obtained 4·76 cubic inches of gas from 100 of the water of a deep spring, of which 3·38 were carbonic acid gas, and 1·38 air, of the same standard as that of the atmosphere. There can, however, be no doubt that the gaseous contents of different springs vary both in quantity and quality.

The following table, based on the experiments of various eminent authorities, exhibits the quantity of different gases which water is capable of absorbing or dissolving at a mean temperature and pressure, the water having been previously deprived of air by long boiling.

	100 c. i. of water dissolve		100 c. i. of water dissolve
Fluoboric acid	70000 c. i.	Chlorine	200 c. i.
Hydrochloric acid	50000	Protoxide of nitrogen	100
Ammonia	48000	Carbonic acid	100
Fluosilicic acid	35000	Carburetted hydrogen	12·5
Hypochlorous acid	20000	Deutoxide of nitrogen	5
Sulphurous acid	5000	Oxygen	4·6
Peroxide of chlorine	2000	Phosphuretted hydrogen	2·14
Cyanogen	450	Carbonic oxide	6·6
Hydroselenic acid	300	Nitrogen	2·5
Sulphuretted hydrogen	300	Hydrogen	1·56

The quantity of each gas dissolved by water is materially dependent on temperature. While in reference to solids, soluble in water, the solubility generally increases with the temperature, that of gases decreases, so that by heating the water to the boiling point, the gas, unless it has entered into chemical combination, is expelled. There is an instance of this exceptional condition in hydrochloric acid gas. When a solution of this gas is boiled, a portion of the acid escapes; but at a certain point of saturation, the water and gas are distilled over together.

Water is decomposed by many substances. Some, like chlorine, take the hydrogen and liberate the oxygen; other substances, like potassium, take the oxygen and set free hydrogen. With the exceptional case of the decomposition of this liquid by electrolysis, oxygen is not set free as a gas, but as it is liberated, it enters into new combinations.

Water plays a most important part in the organic kingdom. It is not only the medium for conveying soluble matters from the earth and air to the vegetable structure, but it is essential to the constitution of vegetable and animal principles. Thus, it forms from 30 to 80 per cent. of the animal tissues; and to its presence the physical properties of these tissues are mainly due. We have found that muscular fibre contains from 66 to 69 per cent. of water, and that an oyster contains 81 per cent. Some of the small jelly-fish (*acalephæ*) contain 99 per cent. of this liquid. Of the fluids of the body, blood contains 78, milk 86, and bile 90 per cent. of water. Its presence in bodies is often indispensable to chemical action, and the removal of it, either modifies or arrests chemical changes. Albumen or gelatin, when deprived of water, may remain unchanged for years; but when containing only their normal proportion of water, they rapidly undergo decomposition. Desiccation, or the deprivation of an organic substance of water, may be regarded as one of the most powerful antiseptic processes. Its remarkable influence on chemical affinity, and on the chemical properties of compounds, has been elsewhere pointed out (*see* page 41). In addition to the illustrations there given, we may here notice a few others. It is well known that lime has a strong tendency to combine with carbonic acid; but unless water is present as an intermediate agent, caustic lime does not easily combine with carbonic acid, to form a carbonate. It is generally stated that caustic lime is procured by heating the carbonate; but the affinity of lime for carbonic acid, when they are once combined, is so strong, that the gas cannot be expelled by heat—according to Faraday, not even by a white heat, unless water is present. Hence, water is not only necessary to the combination of acid and base, but when they are combined, its presence is necessary to bring about their separation. The combination between a gaseous body and a metal does not readily take place, unless water is present (*see* page 41). Thus, while humid chlorine readily combines with pure silver leaf, to form chloride of silver, the combination takes place only slowly and with great difficulty, if the metal and the gas are first thoroughly dried. Phosphorus, it is well known, has a strong tendency to combine with the oxygen of air, and to produce ozone at ordinary temperatures; but if the air is perfectly dry, no ozone is formed; and it has been observed, that dry oxygen is not ozonized by this metalloid. These facts, among numerous others, show the important part which water takes in promoting or modifying the chemical action between bodies, which are known to have strong affinities for each other.

HYDRATES.—*Hydration.* Water is a general and useful solvent. In this respect it is indispensable to the chemist, for by its means he can not only separate substances, but reduce their particles to that degree of tenuity as a result of solution, that they can be brought within the sphere of each other's attraction. Although a perfectly neutral body, it is capable of acting like an acid or a base, and entering into a large variety of combinations. As the water is contained in these compounds in definite proportions by weight, they are called *hydrates* to distinguish them from *hydrides*, of which the element hydrogen is a constituent. In those cases in which the hydrated compounds are crystalline, the water appears to be essential to the crystalline form, and it is therefore called water of crystallization. (*See* p. 31.) Those bodies which do not contain combined water, or which have been deprived of it by artificial processes, are said to be *anhydrous*, and are sometimes, although improperly described as *anhydrides.* They are in fact *anhydrates.* As instances of its combination with *gases* may be mentioned—1, the hydrate of chlorine, a solid compound, consisting of $Cl+10HO$, which crystallizes at 32°, and is reconverted to water and chlorine above this temperature; 2, the crystalline compound produced in the manufacture of sulphuric acid, (NO_4+2SO_2+2HO) resolvable by water or steam into sulphuric acid water and deutoxide of nitrogen. Like an alkali or metallic oxide, water combines with an anhydrous acid to form a hydrate. It thus unites to anhydrous sulphuric, nitric or phosphoric acid; and in reference to the last-mentioned acid, it produces a change in its chemical properties. In this state, acting like a base, it is called basic water. When the acid is once combined with it, the water cannot be again separated by mere heat; the acid and the water are distilled over together. The only method of displacing water in these combinations is to substitute another oxide, such as that of potassium, and then apply heat. Under these circumstances the water is entirely expelled, and it is replaced by an atom of metallic oxide. This replacement sometimes occurs as a simple result of chemical affinity. Thus the three atoms of water in the terhydrate of phosphoric acid, may be replaced by three atoms of oxide of silver, forming yellow phosphate of silver. From these facts it was supposed that water was essential to the acid reaction of a compound, and that none but hydrated acids could unite to bases, to form salts. But certain acids which can be made completely anhydrous by heat, such as the boracic, silicic, and stannic, readily decompose the carbonates, nitrates and sulphates at a high temperature, displacing their acids, and forming new salts with the bases, according to the usual laws of affinity. Anhydrous sulphurous acid will also displace carbonic acid from dry carbonate of soda. (Pelouze et Fremy, *op. cit.* tom. 2, p. 78.) The dehydration of some compounds lessens or destroys their solubility in certain liquids. The silicic and antimonic acids, as well as the oxides of aluminum and zinc in the hydrated state, are easily dissolved by alkalies; but when dehydrated by heat, they become almost insoluble, and can then only be united to an alkali by fusion at a high temperature. Water combines with alkalies without altering or affecting their properties. The hydrate of potassa is a compound of water and oxide of potassium, and has powerful alkaline properties. At a high temperature the hydrate is volatile without any loss of water. In this compound as in the acid hydrates, the water can only be displaced by adding an acid, such as the sulphuric or phosphoric acid, and heating the compound to a high temperature. In some hydrates the water may be displaced by heat alone, as in the case of lime and magnesia. Water forms hydrates with nearly all the metallic oxides, influencing their color and solubility in acids. The hydrated oxide of copper is blue, and the anhydrous oxide is black. The hydrated oxide of this metal when precipitated by potassa from a solution of sulphate of copper (and the alkali is added in some excess) is rendered anhydrous, merely by boiling the liquid. The oxide falls down as a blackish-brown powder. The hydrated suboxide of copper is yellow, and is produced on warming a mixture of sulphate of copper, sugar, and potassa. If, however, the liquid is boiled, the suboxide is rendered anhydrous, and falls down as an insoluble red powder. Up to a temperature of 65° a saturated solution of sulphate of soda deposits on cooling hydrated crystals of this salt. But if heated to the boiling point the salt becomes less soluble by reason of the formation of the anhydrous sulphate, the salt being dehydrated by elevation of temperature. In other cases a heat of 212° appears to be necessary to the production of a hydrate. Precipitate a solution of alum by potassa, and add enough potash to re-dissolve the precipitated alumina; to this alkaline liquid add a solution of silicate of potassa. There is no apparent change until the mixture is heated, when the whole of it sets into a nearly solid hydrated silicate of alumina.

Water combines with the greater number of metallic salts in proportions variable for each salt, and these are not dependent on any general law. Occasionally the same salt is observed to combine with different proportions of water, according to the temperature of the solution. (*See* p. 31.) The color of the salt and its crystalline form are chiefly affected, but its chemical properties do not appear to be changed. The blue crystals of sulphate of copper, and the green crystals of sulphate of iron become of a dingy white, when digested in concentrated sulphuric acid. This is simply the result of dehydration. The color is restored in each case by the addition of water. In some salts the water is combined only as water of crystallization, *e. g.* the sulphates of iron and copper; in other salts, besides this crystalline water, another portion exists in a basic form, *i. e.* intimately combined with the acid. This is seen in the rhombic phosphate of soda, which contains two atoms of soda, and one of water as a base, while there are in addition, 24 atoms of combined or crystalline water. The whole of this water can be expelled by heat, but the basic water with more difficulty than the water of crystallization. The loss of the basic water completely changes the chemical properties of this salt: it converts it into pyrophosphate of soda, which produces a white, in place of a yellow precipitate, with nitrate of silver. It also gives with a solution of acetate of lead, a white precipitate, which is soluble in an excess of the pyrophosphate, while the phosphate of lead is insoluble in the common phosphate of soda.

It has been suggested that some double salts, such as the bisulphate of potassa, may really be compounds of neutral sulphates with water. Thus the bisulphate which is commonly represented as $KO,2SO_3,HO$ may be KO,SO_3+HO,SO_3. This, however, would be inconsistent with the constitution of certain analogous compounds not containing water, such as the bichromate of potassa, $KO,2CrO_3$. Chromic acid is isomorphous with the sulphuric; and if the latter can combine in two equivalents to form a bichromate, it is reasonable to infer that the former can equally combine with two equivalents of acid to form a bisulphate of the alkali, and not a sulphate of potassa and basic water.

The phenomena of hydration as they are witnessed in the combination of water with acids, oxides and salts, are clearly due to chemical affinity. When water is poured on solid sulphuric or phosphoric acid, great heat is evolved, and steam escapes almost with explosive violence. If a small quantity of water is poured on a few pieces of dry hydrate of potassa in a glass tube, the alkali is dissolved, but so much heat is extricated that a small portion of phosphorus applied to the outside of the vessel will melt and take fire. In this experiment, a second hydrate of the alkaline oxide is produced by an additional quantity of water entering into combination. When one part of water at 32° is added to three parts of fresh burnt lime at the same temperature, the water disappears, steam is after a time copiously evolved, the lime becomes hot, falls to a white powder, and is greatly increased in weight. The heat given out in the hydration of lime, has been estimated at more than 570°—sufficiently high to inflame gunpowder. Pelletier observed that in slaking large quantities of lime in the dark, light was evolved as well as heat. The water forms a solid compound with the lime (slaked lime). In these experiments it is considered that the *latent* heat of water (*see* page 128) is set free. This can only be attributed to a direct chemical union of water in a solid form with the substance. Concentrated sulphuric acid (already a liquid hydrate) presents some remarkable and apparently paradoxical results in uniting to an additional proportion of water. If one part of ice is mixed with four parts of concentrated sulphuric acid, the ice melts—great *heat* is evolved as a result of a second hydrate being formed, and the latent heat of the water being set free. But if one part of sulphuric acid is rapidly mixed with four parts of ice, in the same or in another vessel, so intense a degree of cold is produced, that water is frozen in a tube which is placed in the mixture. This result is in accordance with what has been already stated, respecting the large amount of heat absorbed or rendered latent in the liquefaction of ice (p. 128). A hydrate is equally formed in the latter case; but as the ice greatly preponderates, and requires much heat for its liquefaction, it not only absorbs that which is produced as a result of hydration, but much more from all surrounding bodies.

With some acids and alkalies water appears to form no hydrates. Thus the nitrous (NO_4), the fulminic, hydrocyanic, and manganic acids form no definite compounds with water, although they combine with certain bases to produce salts. On the other hand, the presence of an atom of water is essential to the constitution of oxalic acid (C_2O_3). When deprived of it, the acid is converted into carbonic acid (CO_2) and carbonic oxide (CO.) This atom of water admits only of displacement without the decomposition of the acid, by the substitution of an atom of a metallic oxide. Carbonic acid as a gas does not combine with water to form a definite hydrate; and in the liquefied state, carbonic acid is quite insoluble in water. *Liquid* carbonic acid has no action upon litmus, but when the *gas* is dissolved in water, it changes it from blue to red, like other acids. That it forms no acid hydrate may be inferred from the fact, that the blue color of the litmus is restored by boiling the reddened liquid. Carbonic acid, therefore, is in the condition of a gas temporarily dissolved by water. Solution in water appears to be necessary for the manifestation of acid properties on vegetable colors; but, for reasons elsewhere assigned, it is not necessary to suppose that the water undergoes decomposition, and that a new binary compound of hydrogen and a hypothetical radical is produced (p. 86). Pyrogallic acid, as a solid, has no action on litmus; when dissolved in water it reddens litmus paper, but when dissolved in absolute ether, and not exposed to air, it has no reddening action on litmus. In this respect, it resembles liquid carbonic acid dissolved in pure ether. Among bases, ammonia is remarkable for forming no hydrate with water. Every particle of water may be removed, without altering the properties of gaseous ammonia, by simply desiccating it with lime. It has been supposed, that a binary compound of oxygen and ammonium (NH_4) is formed under these circumstances; but of this there is a total absence of proof. (See AMMONIUM.) Such a view assumes, contrary to all experiments regarding the relative affinity of bodies, that hydrogen leaves oxygen to combine with the elements of ammonia, when it is utterly impossible to cause these bodies to unite; and when placed in a favorable state for union, they are rapidly evolved as hydrogen and ammonia.

The phenomena of *osmosis* have been referred by Graham to the hydration and dehydration of the membrane forming the septum, or partition, between two liquids. We have elsewhere referred to the passage of liquids through animal membrane (page 46). The membrane becomes hydrated on the surface which is in contact with the water, but on the side of the saline or viscid liquid, it is not hydrated. On the contrary, hydration here receives a check, and some of the water imbibed by the membrane is actually transferred to the saline liquid, so that there is a continual current inwards or outwards, according to the relative position of the two liquids. (*Phil. Trans.*, June, 1861.) It is a remarkable fact, that while certain bodies will easily traverse the membranous partition, others will not. Substances of a viscid, adhesive, or gelatinous character, whether organic or inorganic (*colloid bodies*), of which animal membrane itself may be considered one, retain certain ingredients, and allow others to pass. It was found by Graham in using parchment-paper, that on placing urine in a vessel provided with such a septum, the urea and salts passed out, but the animal principles were retained. Organic liquids containing small quantities of arsenic, tartar emetic, and even strychnia, were found to yield the respective poisons to water, while the organic substances associated with them did not pass. We have verified this statement by employing a weak solution of arsenic in milk; these experiments show that pure water in hydrating substances, may be employed as a separating agent.

Tests for Water.—When water is in a state of chemical union, its presence is not indicated by any of the usual physical properties of the liquid. Powdered alum contains half of its weight of water, but presents no sign of moisture. In these cases we must resort to a high temperature, and to complex chemical processes, in order to determine its presence and proportion (*see* page 31). When water exists as such in bodies, it is called *hygrometric* water, and it can be easily detected by gently heating the solid in a test tube. The water is expelled, and is condensed in globules on the cold part of the tube. It may be entirely driven off by exposing the substance to a dry current of air. For this purpose the material is inclosed in a glass cylinder, immersed in a water-bath at or below the boiling point. The desiccating apparatus commonly used is connected at one end of the cylinder with a tube containing broken chloride of calcium, while the other end of the cylinder is placed in connection with an aspirator. When the stopcock of this aspirator is opened, air may be made to traverse the whole of the apparatus, first passing through the chloride of calcium tube, in which it is dried. It is thus drawn over the substance in a dry state, at the temperature of the hot water in which it is immersed. When perfectly desiccated, it ceases to lose weight. If the quantity of water is to be determined, a U tube containing chloride of calcium, accurately balanced, should be attached to the other end of the desiccating tube, before connecting it with the aspirator. The increase of weight in this tube, when the experiment is completed, indicates the weight of hygrometric water contained in the substance. The chloride of calcium absorbs and fixes the water as it passes over. In some porous powders the proportion of hygrometric water is very large, amounting to 12 or 13 per cent. Another method of determining the amount of free water in liquids or solids, consists in placing them in a shallow vessel *in vacuo*, over another vessel containing strong sulphuric acid. When the receiver is exhausted there is rapid evaporation in the cold, as the aqueous vapor is absorbed and retained by the sulphuric acid. The amount of water in albumen, or white of egg, is thus determined, and is found to be about 80 per cent.

The tenacity with which hygrometric water fixes itself to solids is remarkable. All fine powders, such as spongy platinum, charcoal, or fine metallic wire, or gauze, filagree silver, and articles of a porous description are, generally speaking, strongly hygrometric, and require a continued application of heat to drive off the water which adheres to them.

Of the tests for liquid water, nothing need be said. It resembles no other liquid, and the means of determining its purity have been already described (page 123). The detection of water in certain liquids, must depend on the nature of the liquid. In alcohol, water may be detected either by its specific gravity, or by adding to it, a small quantity of white anhydrous sulphate of copper. If water is present, the white powder is slowly rendered blue. Fluosilicic acid gas passed into the liquid, also reveals the presence of water, by the separation and deposit of white gelatinous silica. The existence of water in gases, is determined by passing the gas through a vessel containing chloride of calcium, or if acid, through strong sulphuric acid. Any increase of weight in the chloride, or acid, is owing to water.

MINERAL WATERS. SEA-WATER.

When the saline and gaseous ingredients of water, are in such proportion as to give to the liquid, taste, smell, or medicinal properties, it is called a *mineral* water.

Sea-water is a strongly mineralized water; it may be regarded as the accumulation of all the surface-drainage of the earth. It contains, on an average, from 3 to 4 per cent. of saline matter, and this amount does not seem to vary to any great extent, either with the latitude, or with the depth from which the water is taken. Water collected from the surface of the Gulf of Guinea, contained 3·5 per cent., and in the same gulf, when taken from the depth of 4000 feet, it is stated to have yielded 4·5 per cent. of saline residue, showing an increase of only 1 per cent. at this depth. Sea-water taken in N. L., 80°, sixty fathoms under ice, gave 3·54 per cent., and in S. L., 20°, 3·9 per cent.

While carbonate of lime is the principal ingredients in river waters, it exists sparingly in the sea. The chief saline constituent of sea-water is common salt, or the *chloride of sodium:* this forms from one-half to three-fourths of the solid ingredients. The principal salts associated with it, are chloride and bromide of magnesium, with sulphate of magnesia, which give the nauseous bitterness and purgative qualities to the water. Chloride of potassium and sulphate of lime are also found: and as a result of prismatic analysis, Bunsen has lately announced the presence of lithium and strontium, probably existing as chlorides. He detected lithium in less than two ounces of the waters of the Atlantic, collected off the Azores. Iron, lead, copper, and silver, have also been found in sea-water. Silver was detected by M. Malaguti in water taken off the coast of St. Malo, in the proportion of 1 part in 100,000,000, (*Quart. Jour. Chem. Soc.*, 1851, vol. 3, p. 69,) and Mr. Field has lately announced its presence in the waters of the Pacific (*Proc. R. S.*, vol. 8, p. 292).

The proportion of saline matter in the waters of some inland seas is very large. Thus we have found the waters of the Dead Sea in Palestine to contain 24 per cent. of saline matter, of which three-fourths were chloride of sodium. This is six times as great as the quantity contained in the waters of the Mediterranean Sea, in the same parallel of latitude. The water of the river Jordan, which flows into this inland sea, we found to contain no more than two grains of salt to the Imperial gallon, and only a trace of sulphate of lime, while the common salt in the Dead Sea water, amounted to 12,600 grains in the Imperial gallon. This water had a specific gravity of 1·16, and left a considerable incrustation of deliquescent saline matter on spontaneous evaporation. Every part of the human body, excepting bone, readily floated on it. The water of the great Salt Lake in the Rocky Mountains, U. S., is similar to that of the Dead Sea. It has been found to contain 22 per cent. of saline matter, of which 20 per cent. consists of chloride of sodium.

The tidal impregnation of river-water with sea-water may therefore be easily determined, by the discovery in it of a large proportion of the chlorides of sodium and magnesium. Springs are said to be *brackish* when they acquire a taste from the presence of these chlorides. Such springs are met with in countries in which there are vast sandy deserts, also in shallow wells on the sea coast.

The mean specific gravity of the waters of the Atlantic was found to be 1·027; of the Mediterranean, between Gibraltar and Malta, 1·028, and between Malta and Alexandria, 1·029. The waters of the Red Sea, at the northern end of the Gulf of Suez, had a specific gravity of 1·039 (*Proc. R. S.*, Feb. 1855). Admiral King found the waters of the Pacific Ocean to have a specific gravity of 1·026. The influence of river-water on the specific gravity and composition of sea-water, is very remarkable. At the estuaries of all great rivers, the percentage of salt is considerably reduced, and in approaching the coasts of continents, or even of small islands, there is a great diminution in the saltness of the sea. The following summary contains the proportions of saline matter and common salt found, by analysis, in 1000 parts of the waters of various seas: in the North Sea (Heligoland), of saline matter 30·46 (common salt 23·58); British Channel (Schweitzer), saline matter 35·25 (common salt 28·05); Atlantic, saline matter 36·3 (common salt 25·18); the Mediterranean (Usiglio), saline matter 43·73 (common salt 29·42); the Black Sea, saline matter 17·66 (common salt 14·01); the Sea of Azoff, saline matter 11·87 (common salt 9·65); the Caspian Sea, saline matter 6·29 (common salt 3·67).—(Gobel.) The water of the Mediterranean Sea contains more lime than that of the Atlantic, and the proportion of magnesian salts in the Mediterranean water diminishes in proceeding from west to east (Fremy, *Op. cit.* tom. 1, p. 253). The waters of the Baltic Sea contain but a small proportion of saline matter; and the water of the Gulf of Finland is so free from it, that it can be used in place of river-water. The waters of the great lakes in the plains of Tartary, contain large quantities of carbonate of soda and sulphate of soda, with common salt; while those of Thibet contain common salt, with borate of soda.

MINERAL WATERS owe their qualities not merely to the quantity of the ingredients, but to their nature and their intermixture under conditions which it is difficult to imitate by artificial processes. The Tunbridge chalybeate spring contains only seven grains of mineral matter to the Imperial gallon; it owes its properties to the presence of iron, the proportion of which is not more than two grains in the gallon. On the other hand, one of the Vichy springs contains 460 grains of saline matter in the gallon, of which 333 grains consist of bicarbonate of soda. There are, according to O. Henry, soluble silicates of soda and alumina in this water, amounting to forty-four grains in the gallon. In several of the German waters, Bunsen has detected lithium, strontium, and cæsium, in addition to other well-known ingredients. Mineral waters may vary in their solid contents, as much as from 7 to 500 grains in the gallon. They are hot or cold, the former being called *thermal.* The hot springs in Great Britain are few. They are—the waters of Bath, 117°; of Buxton, 84°; of Matlock, 66°; and in Ireland the waters of Mallow, which have a temperature of 72°. On the Continent, some of these waters reach a temperature little short of the boiling point. One of the most remarkable waters for its temperature and composition, is that of the Great Geyser, in Iceland. Examined in 1846 by Bunsen, at a depth of sixty-three feet, this water was found to have a temperature of 260°. A sample of this water, collected on the 16th June, 1856, was observed, at the time of collection, to have a temperature of 190°, the air being 47°. We found this water to contain 106·6 grains of saline matter in the gallon. Of this 19·53 grains consisted of carbonate of soda, 24·42 of chloride of sodium, 14·65 of sulphate of soda, and 48 grains of silica and insoluble matter. There is no doubt that in this, as in the Vichy and other waters, the silicic acid is held dissolved by the alkaline carbonate.

Various classifications of mineral waters have been made. We here give four of the principal varieties, with their special characters:—

1. *Carbonated.*—These abound in carbonic acid associated with variable quantities of the alkalies, soda, potassa, or lime, or with traces of oxide of iron. The waters of Seltzer, Pyrmont, and of Ilkeston, near Nottingham, are of this kind. They are sparkling, and are characterized by an acidulous taste and reaction. 1. They redden an infusion of litmus, but the blue color is restored on boiling. 2. They give a white precipitate with lime-water (carbonate of lime), but the precipitate is redissolved by an excess of the water. 3. When a portion is boiled in a retort, and the gaseous contents are passed into lime-water, carbonate of lime is abundantly deposited. These waters may be *alkaline* from soda (Vichy), or calcareous from lime (Bath, Bristol, Buxton).

2. *Saline.*—These are very numerous. They contain the salts of soda, potassa, and magnesia. Chloride of sodium is generally a predominating ingredient, as in some of the Cheltenham waters. This chloride is generally associated with traces of bromide and iodide of sodium. They are characterized by their taste, and the large quantity of saline matter left on evaporation.

3. *Sulphureous.*—These are known by their having the offensive odor of sulphuretted hydrogen gas, and by their tarnishing or discoloring a piece of silver-leaf, or of glazed card, immersed in them, or by their giving a brown precipitate (sulphide of lead), with any soluble salt of lead. (Kilburn, Harrowgate, Aix-la-Chapelle, Barèges.) The sulphuretted hydrogen appears to be derived from decomposing iron-pyrites, diffused in the strata through which the water flows. The waters, when fresh, have an acid reaction on

litmus, but this disappears on boiling. After a time they deposit a black sediment (sulphide of iron), and lose their offensive smell. We have examined a water of this description from Vancouver's Island, in British Columbia.

4. *Chalybeate* (χάλῦβος, iron).—These waters derive their name from the iron which they hold dissolved. There is scarcely a natural water in which traces of iron may not be found, but the quantity is so minute as not to affect the taste of the water, although so small a portion of oxide of iron as 1-35000th part of the weight of the water, is sufficient to give the strong chalybeate taste possessed by the Tunbridge spring. There are two kinds of chalybeate water—the carbonated and the sulphated. The Tunbridge and Bath waters belong to the carbonated kind; they contain but a small quantity of saline matter (the Tunbridge Chalybeate less than eight grains in the gallon), and they owe their chief property to protoxide of iron, held dissolved by carbonic acid. Hence, although clear when freshly drawn, they become turbid on exposure by the escape of carbonic acid, and they deposit a brown ochreous sediment of hydrated peroxide of iron. The sulphated chalybeates contain a large quantity of sulphate of iron in solution, derived from the oxidation of iron pyrites in the strata from which they issue. We have examined one such spring from Horncastle, in Lincolnshire, and found it to contain, in the Imperial gallon, 263 grains of solid matter, of which 169 grains consisted of the sulphates of iron and alumina. Chalybeate waters abound in the Rhine district, and they are also very numerous in France. In some of the waters of Aix-la-Chapelle, the iron is combined with the crenic and apocrenic acids. One curious fact connected with them is, that they generally contain traces of arsenic. This ingredient may be found in the mineral water itself, but more commonly in the sediment. In France, no fewer than forty-six waters, including the six springs of Vichy and the waters of Mont d'Or and Plombières, are thus impregnated with arsenic. The Vichy water is said to contain the 125th part of a grain of arsenic in a gallon.

The tonic and other medicinal properties of these waters are now considered to be due, at least in part, to the arsenic which they contain. The Wiesbaden water, according to Dr. Hofmann, contains one grain of arsenic in 166 gallons (*Chem. News*, Aug. 11, 1860). The waters of Spa and Kissengen are also arsenical. The arsenic is probably in the state of arsenite and arseniate of iron, and is held dissolved in minute proportions by the carbonic acid of the water. It is precipitated in the sediment with oxide of iron. The arsenic has been probably derived from decomposed iron-pyrites in the strata, and to this cause may be ascribed the presence of arsenic in some of the river waters of this country. It has been found in the water of the Whitbeck, in Cumberland, by Mr. Church (*Chem. News*, Aug. 25, 1860). We have detected it in the water of the Mersey, supplied to a large town, in the proportion of one grain of arsenic in 250 gallons, and Dr. Miller discovered arsenic in a potable water from Suffolk. Mr. D. Campbell and ourselves discovered this mineral in the sediment of some small streams of Derbyshire, and there is but little doubt that if waters traversing mineral districts were examined by chemists, with a view to its detection, arsenic would frequently be found, either in the water or in the sediment. We have detected arsenic in two ounces of dry Thames mud. Its alleged presence in the deposits of boilers may receive an explanation from these facts. It is not found in all chalybeate waters. We have made two analyses of 50 and 100 grains respectively of the ochreous deposit of the Tunbridge water without detecting any trace of arsenic, so that carbonated chalybeate waters do not necessarily contain this mineral.

A carbonated chalybeate-water is known, 1, by its inky taste; 2, by its giving, when boiled, a grayish-green deposit, which becomes ochreous on standing; 3, by its acquiring a pink or purple tint when tincture of galls is added to it; 4, by boiling it with a few drops of diluted sulphuric acid, and adding to it a solution of ferrocyanide of potassium, when Prussian blue is precipitated; 5, paper soaked in an infusion of rose petals, when dipped in this water, acquires a dark color (tannate of iron).

PEROXIDE OF HYDROGEN (HO_2).—This compound was discovered by Thenard, in 1818. It was at one time considered to be water, holding an additional equivalent of oxygen, and was thence called *oxygenated water*, or oxywater. It is, however, a definite compound of oxygen and hydrogen, although resolvable into water and oxygen under some remarkable conditions. It has been obtained free from water and in solution in ether; hence it must be regarded as an independent oxide.

Preparation.—Regnault recommends the following process for its preparation: Peroxide of barium is rubbed in a mortar, with a sufficient quantity of distilled water to make a liquid paste; this paste is added by small portions to a mixture of one part of hydrochloric acid and three parts of water placed in a porcelain vessel immersed in a freezing mixture. The liquid must be kept stirred during the additions. The changes which ensue may be thus represented ($BaO_2+HCl=BaCl+HO_2$). When the diluted acid is saturated, a fresh quantity of concentrated hydrochloric acid is added, and to this another quantity of the peroxide of barium. The operation is repeated until a solution of chloride of barium is obtained, which is saturated for the low temperature to which the mixture is exposed. If the liquid is now immersed in a mixture of ice and salt, the greater part of the chloride of barium is deposited, by reason of its insolubility in water at a low temperature. The small portion dissolved may be precipitated entirely by the cautious addition of sulphate of silver ($BaCl+AgO,SO_3=BaO,SO_3+AgCl$). The precipitates are separated by filtration and pressed. The filtrate is concentrated by evaporation *in vacuo*. For this purpose it should be placed in a shallow vessel over one containing concentrated sulphuric acid. Another and less complex method of preparing this compound consists in adding the paste of peroxide of barium in sufficient quantity to a strong solution of hydrofluosilicic acid. The baryta is precipitated by the acid. The liquid containing peroxide of hydrogen may be separated by filtration, through gun-cotton, and concentrated *in vacuo* by the method above described. The peroxide may be preserved by acidulating it with a small quantity of hydrochloric acid, which, in the diluted state, is not decomposed by it. The peroxide should always be kept in a cool place.

Properties.—Peroxide of hydrogen is a colorless syrupy liquid of a sp. gr. of 1·452. When quite free from water it is not solidified at zero. At temperatures above 60° it begins to be decomposed. If heated, the decomposition takes place rapidly and sometimes with explosion, the compound being converted into water and oxygen ($HO_2=HO+O$). It sinks in water, but is dissolved by that liquid in all proportions, and the aqueous solution is not decomposed until it is heated to above 100°. It bleaches the skin and completely destroys vegetable colors. It is a powerful oxidizer. Potassium, sodium, arsenic, selenium and other simple bodies are rapidly oxidized by it, and the sulphides of copper, silver, antimony, and lead are converted by it into sulphates. It also oxidizes the hydriodic, hydrosulphuric and sulphurous acids. This compound is resolved into water and oxygen, not only by heat but by contact with certain metals or their oxides. It is decomposed by platinum, gold, and silver; and, if the metals are in a finely divided state, with explosion. By mere contact with the oxides of these metals, or with the peroxides of manganese or lead, or by simple admixture with a solution of permanganate of potassa, it is resolved entirely into oxygen and water. It is, however, a remarkable fact that it may remain in contact with phosphorus and phosphorous acid without immediately oxidizing these substances. It has been elsewhere stated (p. 107) that peroxide of hydrogen is considered to be the positive polar state of oxygen (antozone), while the oxygen of the peroxides of manganese and lead is ozone, or oxygen in the negative polar state. The union of the two is supposed to produce neutral oxygen.

Peroxide of hydrogen has been obtained in solution in ether by Dr. Storer. For this purpose he employed peroxide of sodium made by heating sodium cleaned from naphtha, in a platinum dish, and keeping the metal stirred with an iron rod. The peroxide was introduced in small portions into a mixture of 1 part sulphuric acid to 24 water, kept cool by ice. After a few additions, the acid liquid was agitated with successive portions of ether, until the ether ceased to produce a blue color, with a diluted solution of chromic acid. A small quantity of the peroxide of sodium was found to give a large quantity of the compound.—(*Chem. News*, August, 1861, p. 57.) Schönbein has succeeded in impregnating ether with the peroxide by simply introducing a coil of red-hot platinum wire, into a bottle of air, containing a small quantity of ether mixed with water. If this experiment be performed several times, and the liquid shaken each time, it will be found to have dissolved sufficient peroxide, to give a blue color to a solution of chromic acid, and to evolve oxygen with a solution of permanganic acid, with peroxide of lead, or with the hypochlorites. At the same time the ether is oxidized by another portion of oxygen (ozone) which escapes.—(*Ib.*, May, 1860, p. 254.)

Composition.—The analysis of peroxide of hydrogen is easily made by placing a measured quantity of the liquid in a graduated tube over mercury, and then introducing into it some finely powdered peroxide of manganese, wrapped in filtering paper. The liberation of oxygen begins on contact, and the greater the quantity evolved, the stronger the compound. There is no substance known which contains so large a proportion of oxygen as this. It amounts to 94 per cent. by weight, and according to Pelouze, in its maximum of concentration, it will give off 475 times its volume of oxygen. Its constitution is as follows:—

	Atoms.	Volumes.	Weights.	In 100 Parts.	Pelouze.
Hydrogen H ...	1 ...	1 ...	1 ...	5·9 ...	5.88
Oxygen O_2 ...	2 ...	1 ...	16 ...	94·1 ...	94·12
Peroxide of hydrogen	1	1	17	100·0	100·00

It is decomposed by electrolysis, and the quantity of oxygen evolved, is twice as great as that separated from water.

There is no other compound of oxygen and hydrogen known.

CHAPTER XII.

NITROGEN (N=14).—THE ATMOSPHERE.

History.—NITROGEN (from νίτρον, nitre, and γεννάω, to produce) was discovered by Dr. Rutherford in 1772, up to which time it appears to have been confounded with carbonic acid. It was called *Azote* by Lavoisier, a name still retained by the French chemists. This is derived from α, priv., and ζωή, life, owing to the gas rapidly destroying the life of an animal; but it is obvious that such a name would be equally applicable to all the gases. The name assigned to this element by English chemists, is based on the property which it possesses of producing with oxygen, an acid which enters into the composition of nitre. Nitrogen, although found abundantly in the mineral kingdom, is one of the most important constituents of organic substances. A large number of animal, and many vegetable compounds contain it. It forms nearly four-fifths, by weight, of the atmosphere in an uncombined or free state. Among native mineral substances, nitrate of potash contains 14 per cent., and nitrate of soda 16 per cent. of nitrogen. It is a constituent of most fulminating compounds, *e. g.*, the fulminates of mercury, silver, and gold. Ammonia and all its salts contain it in large proportion.

Preparation.—Nitrogen may be obtained by burning phosphorus in a confined portion of atmospheric air. For this purpose, a tall glass jar, open at the bottom, and provided with a stopcock, should be selected: a small porcelain or metallic cup, containing a sufficiency of inflamed phosphorus, is then set afloat in the water-trough, and the jar immediately inverted over it. A quantity of air is at first expelled by the heat: the stopcock is then closed and the combustion goes on for a few minutes; when it has ceased, and the apparatus has cooled, the cup is easily removed by agitating the jar, so as to sink the phosphorus through the water. The residuary gas, which is in nitrogen, should be then thoroughly washed with lime-water, or with a weak solution of potassa. 2. We may procure it without combustion by placing a stick of phosphorus on a cork or in a porcelain capsule on water, and inverting over this a capacious jar of air. In about 48 hours the water will have risen in the jar to the extent of one-fifth, and the residuary gas, when washed with a weak solution of potassa, will be found to be nitrogen in a pure state. 3. Bright iron filings sprinkled in a jar wetted on the inside and inverted over a water-bath, will also yield it—the oxygen in this case being removed by the iron. The residuary gas (nitrogen) is not contaminated with any acid, but it may contain a trace of ammonia, which is easily removed by agitation with water. 4. If, in place of iron, copper turnings or filings are used, the jar being previously rinsed out with strong hydrochloric acid, nitrogen will be equally obtained—the oxygen being entirely removed, while the copper is converted into subchloride. The gas may be decanted and well washed in water. 5. The mode in which nitrogen may be procured perfectly pure is the following: Place in a porcelain capsule, floating in a water-bath, some pyrogallic acid, and pour on the acid a strong solution of potassa. Invert over the capsule a jar of air. The oxygen will be more or less rapidly removed, according to the quantity of pyrogallic acid, and the strength of the solution of potassa. In this case, the carbonic acid as well as oxygen is absorbed by the liquid, so that the residuary nitrogen contains only aqueous vapor, which, if necessary, may be removed from it by dry potash. Other methods for procuring the gas have been suggested, *e. g.* by passing air through a tube containing metallic copper, heated to redness. In this experiment the air is deprived of its oxygen, oxide of copper is formed, and the nitrogen passes over. It has been also recommended to procure the gas by decomposing a strong solution of ammonia by a current of chlorine, but this process is attended with some danger. If the nitrogen is entirely deprived of oxygen by any of the above processes, no red fumes will appear on mixing it with its volume of deutoxide of nitrogen.

Properties.—Nitrogen is a permanently elastic, colorless, neutral gas, with neither smell nor taste: it has no action upon vegetable colors or upon lime-water. It is not dissolved by water, except that fluid has been deprived of its ordinary portion of air by long boiling, when it takes up about one and a half per cent. Its refractive power in regard to light is to that of atmospheric air as 1·034 to 1·000. It is rather lighter than atmospheric air, compared with which its specific gravity is 0·967 : 100 cubic inches weigh at mean temperature and pressure 29·96 grains. (THOMPSON.) Its specific gravity in reference to hydrogen is as 14 to 1. The following experiments will serve to illustrate the properties of this gas. It does not support combustion : 1. A lighted taper, burning camphor, or a flame of ether, when plunged into the gas is immediately extinguished. 2. If quite free from oxygen, inflamed phosphorus will be extinguished in it. These facts prove that in ordinary language, it will neither burn nor support the combustion of other bodies. 3. The neutrality of the gas, if deprived by washing, of any traces of the vapor of phosphorus or of phosphorous acid, may be proved by pouring into it a solution of litmus ; the blue color will remain unchanged. 4. On shaking the liquid with the gas, its insolubility in water, will be manifested by a lighted taper being as readily extinguished after, as before the introduction of the litmus. 5. If into another jar we introduce a solution of chloride of lime, colored with litmus, the blue color will not be discharged —a proof that the gas is not acid. 6. When lime-water is poured into a jar, and the vessel is shaken, the lime is not precipitated. 7. If a solution of potassa is added to another jar, the gas remains undissolved. 8. A piece of caustic potassa moistened and placed in a tube of nitrogen over mercury, produces no absorption or alteration in the volume of the gas. The extinction of burning bodies is common to nitrogen and carbonic acid ; but the experiments 3 to 8 serve clearly to distinguish the two gases, and by 8 they may be separated when mixed. Traces of an acid of phosphorus are sometimes found in the nitrogen obtained by the use of this substance, and the gas may thus appear to have an acid reaction, but as it is procured by the oxidation of iron, no acid is produced.

Potassium will not burn in nitrogen. Allow a stratum of half an inch of water to remain in a jar of the gas. Throw into the jar a piece of potassium ; it will decompose the water, but without combustion.

Although nitrogen is a necessary constituent of atmospheric air, it cannot be breathed in a pure state without destroying life. It does not appear to operate as a poison, but when breathed, it simply induces suffocation, owing to the absence of free oxygen. If it had any directly noxious effects on the body, it could not be breathed by animals in the large proportion in which it enters into the mixture of gases, known as the atmosphere.

Nitrogen is said not to be combustible, but under certain circumstances, it may be made to undergo a kind of combustion, as when electric sparks are passed through atmospheric air, or through a mixture of one volume of nitrogen with two or three of oxygen ; in this case each spark will be attended by the production of a trace of nitric acid, and after some hundred sparks, the blue color of litmus will be changed to red. Here combustion appears to take place in that portion of the gas immediately subject to the action of the sparks ; but the temperature of the surrounding gas is not thus sufficiently elevated to enable the combustion to spread beyond the immediate sparks. This is probably the source of the nitric acid, and of the nitrates found in rain-water after thunderstorms. The nitrogen of the atmosphere is also liable to oxidation, as a result of the action of ozone. (*See* page 105.) Some of the effects ascribed to ozone, have been set down to the combustion of nitrogen.

If a mixture of nitrogen with twelve or fourteen volumes of hydrogen, be kindled as it issues from a small tube, and burned either in common air or in oxygen, water and nitric acid will be formed; so that in this case the nitrogen may be said to undergo combustion by the aid of the elevated temperature of the flame of hydrogen; but it must be recollected that in these cases nitric acid could be produced without the presence of water, and that it may tend to dispose an union which would not otherwise take place. The formation of a trace of nitric acid, when hydrogen is burned in common air, is referable to the same cause. Bunsen has found that by adding to the mixture of oxygen and nitrogen, two volumes of detonating gas (composed of two volumes of hydrogen and one of oxygen), nitrogen may be easily oxidized and converted to nitric acid. If the detonating gas is used in the proportion of from three to five volumes of the mixed oxygen and nitrogen, so much nitric acid is produced, that the mercury in the tube, is dissolved with the evolution of deutoxide of nitrogen. (*Gasometry*, p. 58.)

Much discussion has arisen respecting the nature of nitrogen; and the question has been agitated, whether it is or is not a *simple body*; but although many ingenious surmises have been published on the subject, and many analogies suggested in favor of its being a compound, no experimental proofs have been hitherto adduced. The production of nitrides by combination with certain metals, and the metallization of ammonia, are considered by some chemists to favor the view of its compound nature.

Nitrogen is one of those elementary bodies on which the electric current appears to exert no influence. According to Faraday's researches, nitrogen, when under the influence of the current, has shown no tendency to pass in either direction.

Equivalent and Compounds.—The equivalent weight of nitrogen is 14, and its volume equivalent is 1. In the free state, it is remarkable for its neutrality or indifference to combination. In the nascent state it readily unites with hydrogen and oxygen, forming ammonia, and, in some cases, nitric acid. It forms also compounds with carbon, chlorine, and iodine, but only as a result of complex chemical changes. When combined, it is remarkable for its instability, since slight physical causes will lead to its sudden separation with explosion, from many of its combinations. Fulminating substances frequently owe their properties to the suddenness with which this element is liberated.

Tests.—Nitrogen-compounds, such as nitric acid and ammonia, are easily recognized by appropriate tests. The only difficulty connected with the detection of nitrogen, is in reference to its presence in organic substances. It is, however, readily converted into ammonia, and from the production of ammonia, we infer the existence of nitrogen. For this purpose, the substance dried and powdered is mixed with its bulk of soda-lime (a mixture consisting of two parts of hydrate of lime, and one part of hydrate of soda). On the application of heat to the mixture, ammonia is evolved. This is known by its odor, and its volatile alkaline reaction on test-paper, as well as by its special chemical characters. (*See* AMMONIA.) Another method consists in forming a carbon-compound (cyanogen). The substance powdered is introduced into a closed tube, with a small portion of potassium or sodium, the metal being placed below. The mixture is then heated to fusion, and, when cold, the dark residue is lixiviated in water. The aqueous solution filtered, acidulated with diluted sulphuric acid, and tested with a solution of persulphate of iron, will yield Prussian blue (a compound of cyanogen and iron.) The detection of a cyanogen-compound proves that nitrogen must have been present in the organic substance.

THE ATMOSPHERE.—It will be understood from the preceding remarks, that atmospheric air is a mixture of gases, in which nitrogen predominates.

Besides, nitrogen, which forms nearly four-fifths, the other principal ingredient is oxygen, constituting about one-fifth; and in addition to these, there are comparatively small quantities of carbonic acid, aqueous vapor, sulphurous acid, ammonia, and other gases, as well as organic matter. The term atmosphere (from ατμὸς, vapor, and σφαῖρα, sphere), is applied to the great aërial ocean which surrounds the earth, and extends, in varying degrees of density, about forty-five miles from its surface. Large as this may appear, it represents only 1-160th part of the earth's diameter;—in a globe of forty feet diameter, this would be equivalent to a thickness of only three inches. The term atmosphere is appropriate, inasmuch as it is the receptacle of all the gases and vapors, organic or inorganic, which are constantly escaping from the surface of the earth and sea.

Properties.—The physical and chemical properties of the air are those of its two principal constituents, oxygen and nitrogen; the active properties of oxygen being modified by dilution with nitrogen. Air is a transparent, colorless, elastic, tasteless fluid, and, as its two constituents are permanent gases, it has not yet been liquefied by cold or pressure. It has been condensed to a degree but little inferior to that of water (1-675th part of its original volume), without undergoing any change in its physical condition (page 74). Heat simply expands it (page 76), and, within certain temperatures, with great uniformity. The nitrogen has no positive properties; oxygen is the principal chemical agent, and is largely consumed in combustion and respiration (page 88). The oxygen thus consumed is replaced by an equal volume of carbonic acid, and this in its turn is absorbed and decomposed by the green parts of vegetables under the influence of solar light, so that the carbon is fixed in the vegetable structure, and the oxygen is evolved either in its common or allotropic state. The animal and vegetable are thus proved, in reference to the atmosphere, to have a compensating relation to each other. Air is dissolved by water, but the oxygen is taken up in larger proportion than nitrogen (page 129). It is this which imparts a fresh, aërated taste to water. The proportion of air dissolved, is subject to variation, but in natural spring waters it is seldom less than two cubic inches in one hundred of water. It is expelled by boiling, congelation, or the removal of atmospheric pressure, as by placing a glass of spring water under the receiver of an air-pump and exhausting the vessel. The air is seen to escape in small bubbles. Owing to the diminution of pressure, water at lofty elevations is less aërated than at the level of the sea, and, by reason of the deficiency of air, the lake-water of high mountainous districts, is not fitted to support the existence of fish. Air adheres more or less to all solids, and it is especially contained in porous solids. A stick of charcoal sunk in water by a leaden weight, and placed *in vacuo*, yields a large quantity of air, which issues in torrents from the broken ends. A piece of pumice, or an egg, sunk in a vessel of water, presents a similar phenomenon. Even the smooth and polished surfaces of metals, may thus be proved to have a film of air adherent to them.

In *combustion*, the oxygen alone is consumed, the nitrogen is set free and mixes with the carbonic acid produced at the expense of the oxygen. Air is therefore rapidly contaminated by this process, and in a confined space, the nitrogen and carbonic acid, as a result of the heat of combustion, accumulate in the upper part of the vessel or apartment. Neither of these gases is respirable, and neither will support ordinary combustion. The following experiments will illustrate the deterioration of air under these circumstances. Fix three wax tapers to a stout wire placed upright, and about three feet in height, so that one is at the upper part, one at the lower, and the third in the middle. Light the tapers, and invert over them a tall stoppered shade, leaving a slight space for the entrance of air below. The accumulation of deoxidized air (nitrogen) and carbonic acid in the upper part of the shade, will be indicated by the early extinction of the upper and middle tapers, while the lower one will continue to burn. If, when the lower taper is burning dimly from impurity of the air, the stopper is removed from the shade, a current of air is immediately set up, the gaseous products of combustion are carried off, and the lower taper will burn with a brighter flame. This experiment establishes the necessity for a rapid removal of the products of combustion, and the results are equally applicable to the contamination of air by the respiration of animals. Fix in the stoppered aperture of a bell jar, by means of a closely-fitting cork, a glass tube, about an inch in diameter. The tube should rise several inches above the level of the jar, and should reach on the inside to within two inches of its base. Mount in a plate two pieces of wax taper, one sufficiently tall to reach nearly to the top of the jar when placed over it, the other so short, that when ignited, the point of the flame only will be inclosed by the open end of the glass tube fixed in the jar. Light the tapers and invert the jar over them, not pressing it down closely at the base. The tube should be so adjusted to the short taper, as to act like a chimney to it, care being taken that it is not touched by the flame. In a short time, if the cork is well fitted, the tall taper will be extinguished, but the short taper will continue to burn. In the one case, the products of combustion are not carried off, in the other they are, and the supply of air is continually renewed. As a proof of this, if we hold over the chimney-tube a small gas-jar, the deposition of water on the glass will be apparent, and after a time, the presence of carbonic acid may be proved by pouring lime-water into the jar. (The production of carbonate of lime will be indicated by a milky appearance of the lime-water.) The principles of the ventilation of dwellings are based on a proper adjustment of the supply of pure air for combustion and respiration, and a provision for the complete removal of the products as they are formed. In the burning of coal-gas the production of sulphurous acid may be an additional source of noxious impurity.

When combustion takes place in rarefied air, as when a candle is placed under a receiver from which the air has been partially removed by the air-pump, the flame is elongated, becomes less luminous, and is soon extinguished. According to observations made by Dr. Frankland, in 1859, on the summit of Mont Blac, it appears that at this elevation the amount of combustible consumed, is as great as at the level of the sea, although the light emitted by a burning candle is considerably less.

Air is usually taken as the standard of specific gravity for gases, being, for this purpose, 1·000. It is also the standard for refraction, specific heat, and other properties of gases. One hundred cubic inches of dry air at mean temperature (60°), and mean pressure (30 inches), are considered to weigh 31 grains. This nearly corresponds to the sum of the weights of the constituent gases, having regard to the proportions in which they are mixed. Air is about 815 times lighter than its volume of water, at 60°. Compared with hydrogen its density is as 14·4 to 1. The weights of 100 cubic inches of any gas or vapor may be determined by multiplying the specific gravity of the gas or vapor by 31, the weight of 100 cubic inches of air. Thus: nitrogen has a sp. gr. of 0·967 and $0·967 \times 31 = 29·98$ grains, the weight of 100 cubic inches of this gas.

Pressure of the Atmosphere.—Owing to the gravitating force of the atmosphere and the great elasticity of its constituent gases, the lowest stratum—that which is in contact with the surface of the earth, and in which warm-blooded animals live, is highly condensed. The pressure of the atmosphere at the level of the sea, is equal to 15 pounds on every square inch, or about 2216 pounds on each square foot. It is calculated that one cubic inch at the surface, would expand into 12,000 cubic inches at the extreme limit of the atmosphere (45 miles). The proportionate increase in volume at different elevations, as the result of the decrease of pressure, is given in the subjoined table. It will be perceived that at a height of only 2·705 miles (14,282 feet), the atmosphere loses one-half of its density; in other words, one volume at the surface would expand into two volumes at this elevation. So rapid is the decrease of density, that while one-half of the mass of the atmosphere is within three miles of the surface, four-fifths of it are within eight miles, leaving only one-fifth for the thirty-seven miles above this elevation. While the height increases in arithmetical progression, the increase of volume (or decrease of density) follows a geometrical ratio :—

Height above the sea in miles.	Volume.	Height above the sea in miles.	Volume.
0	1	10·820	16
2·705	2	13·525	32
5·410	4	16·230	64
8·115	8	18·935	128

The temperature of the atmosphere diminishes about 1° for every 350 feet of ascent, the cause of which is partly referable to the increased capacity of air for heat in proportion as its density diminishes, and partly to the circumstance that the atmosphere is chiefly heated by contact with the earth. The line of perpetual congelation gradually ascends from the equator to the poles. At 0° latitude it is stated to be 15,200 feet; at 60°, 3,818; and at 76°, only 1000 feet.

If a tube three feet long is filled with mercury, and inverted in a mercurial bath, the metal will fall in the tube until its height from the surface of the bath is equal to about 30 inches. If placed under a receiver and the air is withdrawn, the mercury will fall in the tube. On readmitting the air it will again rise. It is therefore obvious that this column of mercury is supported in the tube by the pressure of the atmosphere on the surface of the liquid metal in the bath. From this experiment it will be easy to calculate the exact amount of pressure on the lowest stratum of air. This has been already stated to be equivalent (in round numbers) to 15 pounds avoirdupois on every square inch of surface. In reality, however, the pressure, assuming the mean height of the barometer to be 30 inches, is 14·6 pounds on the square inch—a result which is thus obtained: The weight or gravitating force of the atmosphere, is proved, by the experiment above-mentioned, to be exactly equal to the weight or gravitating force of a column of mercury thirty inches in height. A column of this metal, the base of which would be equal in area to a square inch, would consist of thirty cubic inches. The specific gravity of mercury being 13·5, the weight of a column of 30 cubic inches will represent the gravitating force of the atmosphere on the area of a square inch. A cubic inch of mercury weighs 3408·183 grains (252·458× 13·5—the weight of a cubic inch of water multiplied by the specific gravity of the metal), and therefore 30 cubic inches would weigh (3408·138×30)= 102245·49 grains, or 14·6 pounds avoirdupois. Hence this may be taken as the true amount of atmospheric pressure when the barometer is at its mean height. A column of water 33 feet in height, or a column of air 45 miles in height, each having the area of a square inch, would be equal in pressure to a column of mercury 30 inches in height. These different heights correspond to the respective specific gravities of the liquids.

The influence of this pressure on the volume of gases may be easily proved. Place a light caoutchouc-ball under the receiver of an air-pump and withdraw the air. The ball will increase in size as the air is withdrawn—the air which is confined within the ball acquiring a power of expansion by the diminution of pressure. If the mouth of a wide glass jar is well secured with a layer of stout caoutchouc, and the jar is placed under the receiver, on the removal of the air the membrane will be enormously distended by the expansion of air in the jar, and may ultimately burst. Invert in a gas-jar, a graduated tube containing water, colored with sulphate of indigo, leaving two cubic inches of air at the top. Place this under the receiver. As the air is withdrawn the air in the tube will expand, and, when the barometer marks 15 inches, it will be found that the two cubic inches will occupy the space of four, thus showing that by the removal of half the pressure the air has been doubled in volume. This experiment proves that the density of the air is in a direct ratio to the compressing force. With the pressure of half an atmosphere the volume is doubled, and with a pressure of two atmospheres it is reduced to one-half. It is the same for all gases and vapors (above the boiling point of their liquids), whatever may be their respective specific gravities.

A well-ground receiver, when the air is removed from the interior, is pressed with such force to the air-pump plate that it is impossible to move it. But this presssure may be made visible by the following experiment. Close one end of a stout glass-cylinder four or five inches in diameter, with a strong layer of sheet India rubber, and apply the other end, which should be well-ground for this purpose, to the plate of the air-pump. As the air is gradually withdrawn, the rubber will be pressed downwards, filling the interior of the vessel, and it may ultimately burst. If for the rubber we substitute a layer of wet bladder, and allow this to dry, on placing the glass on the air-pump plate, and rapidly exhausting it, the bladder will be burst with a loud report, as a result of the air rushing into a partial vacuum. Owing to the great amount of this pressure, receivers and other vessels intended for exhaustion should be made of stout glass, and rounded at the top.

As in all fluids, the pressure is equal in all directions. The pressure downwards is proved by the preceding experiments. The force of the pressure *upwards* may be proved by the following simple experiment: Fill a well-ground gas-jar, about twelve inches long and three or four inches wide, with water. Place over this a square of stout writing-paper, and, pressing it firmly to the water, suddenly invert the jar. The heavy column of water will be for a time supported by the atmospheric pressure upwards on the outer surface of the paper. Make a chemical vacuum by pouring into a well-ground jar, containing carbonic acid, a small quantity of a strong solution of potash, and cover the jar immediately with plate-glass. On agitating the jar the gaseous contents will be removed, and the cover will be firmly fixed to the jar by atmospheric pressure. In whatever position the jar may be held the cover will remain equally fixed, showing equality of pressure in every direction. From the powerful effects thus produced when the air is removed from one surface, it may be conceived that nothing could withstand this pressure unless it were equal in all directions, and thus completely neutralized.

Composition. Eudiometry.—Numerous analyses of the air made by chemists of repute, show that the proportions of nitrogen and oxygen are not strictly uniform, either for the same place or for different localities. The proportion of oxygen varies from 20 to 21 per cent. The amount of *oxygen* by volume is readily determined, by the adoption of any of the methods for separating it described under nitrogen (page 141), provided care is taken to provide for this purpose an accurately graduated gas tube and a mercurial bath. Among these, the process described under 5, is preferable to the others. Phosphorus cast in small balls is sometimes used, but unless the vapor of phosphorous acid (produced as a result of oxidation) is removed by a ball of potash, before the volume of nitrogen is read off, there will be a considerable error in the results. Liebig has advised, in place of phosphorus, a ball of papier mâché, saturated with a concentrated solution of pyrogallate of potassa. The absorption takes place slowly but completely, particularly if the ball be once renewed. After this absorption, the gas must be dried by a ball of potassa, containing as little water as possible.—(Bunsen, *Gasometry*, p. 79.) In this case the pyrogallate of potassa, and dry potassa, remove the oxygen, carbonic acid and aqueous vapor, leaving nothing but nitrogen. The temperature should be noted both at the beginning and end of the experiment.

The ordinary volumetric method of analysis, is based on the admixture of a quantity of pure hydrogen with air, and its conversion to water, by any of the usual processes, at the expense of the oxygen contained in the air under examination. As it is well known that oxygen represents one-third of the volume of the combined gases (WATER, page 116) the division of the loss by 3, will at once give the quantity of oxygen present in the air. The air and hydrogen, in about equal proportions are introduced into a graduated glass-tube placed over mercury, or into a syphon-tube containing mercury, especially constructed for this purpose; and the gases are then either detonated by the electric spark, or are slowly combined by means of a ball composed of spongy platinum and clay, introduced through the mercury into the tube. The gases should be allowed to diffuse thoroughly, before any attempt is made to combine them. The following experiment on the air of London, will illustrate the principle of this operation. The air examined amounted to 35 parts by volume. To this quantity 42 parts of hydrogen were added. The mixed gases, therefore, amounted to 77 parts. A ball of spongy platinum was introduced into the mixture, and in two hours, combination was complete. It was found that only 55 parts of gas remained in the graduated tube. The loss, therefore, as watery vapor was 77—55=22; and one-third of this must have been oxygen. Therefore 22÷3=7·33 for the proportion of oxygen in the 35 measures taken; and 35 : 7·33 : : 100 : 20·94 oxygen. Deducting these figures from 100, the air examined had this composition in 100 parts: oxygen 20·94; nitrogen 79·06. The use of spongy platinum for the combination of the gases, appears to be less liable to fallacy, than the detonation of the mixture by the electric spark. Bunsen has shown, that unless great precautions are taken, so much nitric acid may be formed in the presence of oxygen and hydrogen by the combustion of nitrogen, as to lead to a serious fallacy in calculating the amount of oxygen. (*Gasometry*, page 60.) On the other hand, the pyrogallate of potassa, as an absorbing liquid, was found to give very accurate results.

To this kind of analysis the term *eudiometry* (εὖ, δίον, and μέτρόν, measure of the purity of the air), has been applied, since the healthiness of localities was erroneously supposed to depend on the proportion of oxygen present. Eudiometric tubes, finely graduated and connected with bottles containing a liquid for the absorption of oxygen, were formerly employed. The air contained in the tubes was exposed to the eudiometric liquid, and the amount of absorption was ascertained by opening the bottle under water. A solution of sulphide of potassium, or of protosulphate of iron saturated with deutoxide of nitrogen, was formerly used for this purpose. Such methods of analysis have been long since abandoned.

As errors frequently arise in reading and correcting the volumes of gases, owing to the variable influence of pressure, temperature, and other causes, chemists have given some attention to the discovery of a method for determining the oxygen and nitrogen by *weight*, in one operation.

This has been successfully accomplished in the analysis of air, performed by Dumas and Boussingault. The operation is very simple. Air, deprived of its carbonic acid, and aqueous vapor, by causing it to pass through a series of tubes, some of which contain concentrated sulphuric acid, and others, a saturated solution of potassa, is finally made to traverse a balanced tube containing metallic copper, heated to redness. It is here entirely deprived of its oxygen. By opening a stopcock communicating with a large glass globe in a state of vacuum, the deoxidized air, or nitrogen, is collected in this vessel, which acts as an aspirator. When filled, the glass globe is removed and weighed. It is now brought to a state of vacuum, and again weighed. The difference in weight represents the amount of nitrogen, while the increase in weight in the balanced tube containing the copper, gives the amount of oxygen. All the other constituents of air, excepting oxygen and nitrogen, are excluded by this method of analysis. The results thus obtained are in close accordance with those determined by other chemists. Air is thus found to be constituted by volume and weight:—

	By Volume.	By Weight.
Oxygen	20·80	23·10
Nitrogen	79·20	76·90

Carbonic acid, although in small proportion, is a universal constituent of air. It has been found at all elevations at which it has been sought for, and may be readily detected by causing a large quantity of air to pass through a tube or vessel, containing a solution of lime or baryta; or by simply exposing to the atmosphere, a solution of the alkaline earth in a shallow glass dish. A white precipitate, or an incrustation of carbonate of lime or baryta, is obtained after some hours. The presence of *aqueous vapor* in the air is known by the deposition of water on the exterior of a glass-vessel in which ice has been placed, or by exposing to a current of air, fused chloride of calcium in a glass tube. In this case the water is absorbed, and the chloride gradually passes to the liquid state.

Various methods have been adopted for the purpose of determining the proportions of carbonic acid and aqueous vapor. In reference to the former, M. Thenard employed a solution of baryta; and from the amount of carbonate of baryta, obtained by agitating this liquid with a measured volume of air, he concluded that the proportion was about 1-2000th part, or one cubic inch in two thousand cubic inches of air. The plan more recently adopted by Boussingault, Regnault, and other chemists, is based on the separation and weighing of carbonic acid and aqueous vapor in one operation. By means of a large aspirator, the air is made to traverse a series of balanced tubes filled with broken pumice, impregnated with concentrated sulphuric acid, and after having been thus deprived of *water*, the air traverses another series of balanced tubes, also filled with pumice strongly impregnated with a concentrated solution of potassa. These tubes arrest the *carbonic acid.* Any change of temperature in the contents of the aspirator, during the performance of the analysis, is accurately noted. It will be obvious, that by repeatedly filling the aspirator any quantity of air may be thus made to pass through the balanced tubes, and the first of the series may have a length of vulcanized tubing so adjusted to it, as to bring the air from any particular spot. After the completion of the experiment, the amount of aqueous vapor is known by the increase of weight in the sulphuric acid tubes; and the amount of carbonic acid, by the increase in the potassa tubes. Reducing these quantities to volumes, and dividing the whole amount of air by the volumes, the proportions of both of these constituents may be determined.

The quantity of *carbonic acid* amounts to from 3·7 to 6·2 measures in 10,000: or on an average about 1-2000th part by volume. According to Saussure, the proportion varies with the season; the air in a meadow, in August, contained 0·000713; in January, 0·000479; in November, in rainy and stormy weather, 0·000425. Dalton estimates the carbonic acid at 0·001; Configliachi, the maximum at 0·008; and Humboldt (probably an excess) at 0·005 to 0·018. Saussure and Gay Lussac found the usual proportion of carbonic acid in the air from the summit of Mont Blanc, and 4000 feet above Paris. Beauvais found scarcely a trace of carbonic acid in the air over the sea off Dieppe, but the usual proportion inland.—(L. GMELIN.)

Carbonic acid is in such small proportion in air, that lime-water indicates no trace of its presence in 200 cubic inches contained in a closed bottle. In air taken from low and confined situations, as wells and cellars, the carbonic acid may amount to from 3 to 10 per cent. Air suspected to be strongly impregnated with this gas, may be thus tested. Fill a long, narrow tube with lime-water, and invert it on the water-bath; pass up through the lime-water a few cubic inches of the suspected air. If the carbonic acid is in undue proportion, this will be made evident by the lime-water acquiring on its surface a milky appearance, owing to the production of carbonate of lime. Carbonic acid is stated to be contained in air, in greater proportion in summer than in winter—at night, than by day—in cloudy, than in fine weather—in dry, than in wet weather; but there is no doubt that the amount of this gas, is kept down partly by its great solubility in water and its removal by rain; and partly by vegetation. In the latter case the gas is decomposed, and oxygen is set free. The great sources of carbonic acid are combustion, respiration, putrefaction, decay, and fermentation.

The relative quantity of *aqueous vapor* in the atmosphere, is subject to much variation. From the experiments of Saussure, Dalton, and Ure, already referred to, it appears that 100 cubic inches of atmospheric air at 57°, are capable of retaning 0·35 grains of watery vapor; in this state, the air may be considered at its maximum of humidity. It would also appear that all gases not condensible by water, take up the same quantity of water when placed under similar circumstances, and that it consequently depends, not upon the density or composition, but upon the bulk of the gas. From Dalton's researches, it may be concluded that the vapor forms an independent atmosphere, mixed, but not combined with air.

The proportion of water diffused as a vapor in a gas, depends upon temperature, and not upon the pressure of the atmosphere. The higher the temperature, and the dryer the atmosphere, the larger the quantity of vapor taken up. As it is the same at mean temperature, in all gases, the proportions have been tabulated, and will be found in the APPENDIX. The quantity by volume contained in air at 52°, is estimated to be 1·42 per cent., or about 5 to 12 grains in a cubic foot. In air already saturated with it there is no evaporation. The presence of aqueous vapor in air, is not only necessary to vegetation, but is indispensable to the respiration of animals. Dry air produces an irritative effect on the air passages and lungs.

Ammonia is known to be a constituent of air, but in very small proportion. It is detected by passing a large quantity of air through a vessel containing hydrochloric acid diluted with water. After operating on a considerable quantity of air, chloride of platinum is added to the acid liquid, which is then evaporated, and the ammonio-chloride of platinum collected, dried, and weighed. From this weight the proportion of ammonia in air is deduced. M. Græger found that the quantity was 0·000,000,333 of the weight of air. Kemp found a larger proportion, namely, 0·000,003,88, and Fresenius 0·000,000,133. Horsford, of the United States, has endeavored to determine the proportion in America, and has arrived at the conclusion that a million parts of air by weight contain from 1 to 42 parts of ammonia, the minimum amount being found in December, and the maximum in August. It is probable that this constituent, although small, may serve an important purpose in reference to vegetation.

The great variation in these results, shows that the proportion of ammonia cannot be accurately defined. It may be described like some acid vapors, as existing only in traces.

Organic matter is found in the atmosphere, especially in inhabited localities, or where animal or vegetable matter is undergoing decomposition. It is this which gives the foul odor to closely confined rooms, in which many persons have breathed without due ventilation. Dr. Angus Smith has endeavored to determine the proportion present in air, by noticing how many measures of air were required to remove the color from a weak standard solution of the permanganate of soda, or potassa. The larger the amount of organic matter, the smaller the quantity of air required to cause the permanganate to lose its characteristic pink color. He has called this instrument the *sepometer*. He states that he has found a considerable difference in the results of experiments on the air of towns, of the country, and of the sea-coast. The state of ventilation in a room can, according to him, be determined by it, and it has enabled him to register degrees of impurity in air, which could not be detected by the smell.

He found that equal quantities of a standard solution of the alkaline permanganate were decolorized by 22 measures of air, from the high ground of Lancashire—by 9 from an open street in Manchester—by 5·5 from some small houses on the Medlock—by 2 from a close carriage of passengers, and by 1 from the back yard of a house in a low and ill-ventilated neighborhood.

The results of his experiments show that on some of the Swiss lakes, and on the German Ocean, sixty miles from land, the sepometer indicated, in the air, but a small amount of organic matter, or of matter capable of decolorizing the test solution. The maximum effects were produced by air from a house kept close, and from a pigstye recently uncovered.

The operation of the permanganate, clearly depends on the oxidation of organic matter, probably as a result of the ozone associated with this salt (page 103). There can be no doubt that organic matter possesses the property here ascribed to it, and that in localities where ozone is least to be detected in air, the largest amount of permanganate will be deprived of its color. At the same time, the results are open to the objection that sulphurous acid, sulphuretted hydrogen, and other deoxidizing compounds, will equally discharge the color of an alkaline permanganate, whether organic matter is or is not present. Hence provision should be made for the removal of these agents before the air is submitted to this method of testing.

The composition of the air, excluding ammonia, organic matter, and other casual constituents, may be thus stated, for 1000 and 100 parts by volume respectively:—

	In 1000 vols.	In 100 vols.
Oxygen	208·0	20·80
Nitrogen	777·0	77·70
Aqueous vapor	14·6	1·46
Carbonic acid	0.4	0.04
	1000·0	100·00

The air, not a chemical compound.—The proportions of oxygen and nitrogen nearly approach to 1 vol. or 2 eq. of oxygen, and 4 vol. or eq. of nitrogen. This ratio, however would give a percentage of 20 of oxygen to 80 of nitrogen, proportions that are never found. The gases are therefore not combined in equivalents, either by weight or volume. As an additional proof that the air is a mere mixture, the following experiments may be adduced. Remove the oxygen from a jar of air by phosphorus or iron-filings, and then restore the loss by an addition of pure oxygen. The gases will diffuse or enter into mixture without any of the phenomena that accompany chemical union, and a candle will burn in this mixture, as it does in air. There is no alteration in volume, no evolution of heat or light, and the specific gravity, magnetism, refractive power, and solubility in water, of this mixture, correspond to the mean specific gravity, and other properties of the constituents. The solvent power of water is such as would be exercised upon a mixture, and not upon a chemical compound of the two gases. Thus oxygen is dissolved in larger proportion than nitrogen, and the difference nearly corresponds to the difference existing in the solubility of the two gases, in their separate states. Thus, according to Regnault, of 100 parts of air dissolved by water, the oxygen is to the nitrogen as 32 to 68, instead of 20·8 to 79·2; while the solubility of each gas gives a calculated proportion of 31·5 to 68·5. Thus:—

	Solubility.				Calculated Solubility.	Actual Solubility.
Oxygen . . .	0·046	($\frac{1}{5}$)	= 0·0092	or	31·5	32
Nitrogen . . .	0.025	($\frac{4}{5}$)	= 0·0200	or	68·5	68
Air in water					100.	100.

Lastly, metals and metalloids act upon air in the same manner as if the gases were free. Potassium, sodium, lead in the melted state, phosphorus, and deutoxide of nitrogen, take the oxygen of air, just as they take oxygen in the free or uncombined state.

It has been supposed that the comparative uniformity of composition in all parts of the globe, and at all elevations above the sea, could only admit of explanation on the theory that the two gases were chemically combined. The laws of diffusion, however, sufficiently account for the uniformity of mixture (page 79), while at the same time, the ascertained differences in the proportions of oxygen and nitrogen are not reconcilable with the theory of their being chemically united. Taking the proportion of oxygen by weight elsewhere given (page 149), namely, 23·1 parts in 100, the following are comparative results of the analysis of air in different localities:—

	Wt. of O. per cent.		Wt. of O. per cent.
Paris (April to Sept. 1841) .	23·07	Guadaloupe (W. I.) . .	22·97
" another observation .	23·13	Copenhagen . . .	23·01
Bern (Switzerland) . .	22·95	Elsinore	23·03
Faulhorn (18,800 feet) .	22·98	German Ocean . . .	22·86

Other comparisons may be instituted in reference to its composition by volume. Assuming the average proportion of oxygen by volume to be 20·80, the following results have been obtained:—

	Vol. of O. per cent.		Vol. of O. per cent.
Paris	20·93	Mont Blanc (6000 feet) .	20.20
London level of sea . .	20·92	" summit (16,000 feet)	20·96
" 18,000 feet elevation	20·88	Simplon (6000 feet) . .	19·98
Heidelberg	20·95	Wangen Alp (4000 feet) .	20·45
Berlin	20·90	Aerial ascent (9000 feet) .	20·70
Madrid	20·91	In Manchester, . . .	20·88
Geneva	20·90	In open places . . .	21·10
Lyons	20·91	In open country . . .	21·00
Helvellyn (3000 feet) . .	20·58	In crowded rooms . .	20·42
Snowdon (3570 feet) . .	20·65	Polar sea	20·85

During the period of about fifty years, within which accurate analyses of the atmosphere have been made, there has been no greater difference in the proportions of its constituents, than that which is above shown to exist between any two localities at the present time. There has been no apparent diminution in the amount of oxygen and nitrogen.

Tests for Air.—These are necessarily included in the tests for oxygen and nitrogen. The presence of nitrogen so affects the combustion of bodies in air, that the burning of a candle furnishes a good test of the atmospheric mixture. The red acid vapor produced by adding to air, deutoxide of nitrogen, and the entire removal of oxygen by the pyrogallate of potassa, with the negative properties of the residuary gas, nitrogen, are sufficient to identify the mixture under all circumstances.

CHAPTER XIII.

COMPOUNDS OF NITROGEN AND OXYGEN. NITRIC ACID.

THERE are five compounds of nitrogen and oxygen—two neutral gases and three acids. In these compounds the equivalents of oxygen undergo a regular arithmetical increase.

They are as follow:—

Neutral.		Acid.	
Protoxide	NO	Hyponitrous acid	NO_3
Deutoxide	NO_2	Nitrous acid	NO_4
		Nitric acid	NO_5

1. PROTOXIDE OF NITROGEN.—*Nitrous Oxide* (NO).—This gaseous compound was discovered by Priestley in 1776: but its properties were not fully known until after the researches of Davy in 1800.

Preparation.—The gas may be procured by heating in a glass retort the crystals of pure nitrate of ammonia. The temperature should not exceed 400°, and the salt, which speedily melts, should be kept in a state of gentle ebullition. The gas, being very soluble in water, in order to prevent loss, should be collected in a water-bath, containing tepid water. In this case, however, it always becomes mixed with much air on cooling. The salt is entirely resolved into water and protoxide ($NH_3,HO,NO_5,=2NO+4HO$). One ounce of the nitrate will give 500 cubic inches, or nearly two gallons of the gas.

If, during the process, the liquefied salt should be overheated, the gas comes over with explosive violence, sometimes breaking the retort, or leading to the production of nitrogen as well as deutoxide, and thereby rendering it impure. The production of copious white vapors in the retort is a sign that the proper heat has been exceeded. If the nitrate contains hydrochlorate of ammonia chlorine will be evolved, and impart to the gas its peculiar odor as well as bleaching properties. The presence of hydrochlorate in the nitrate of ammonia may be known by the solution of this salt giving a white precipitate with a solution of nitrate of silver. If any deutoxide of nitrogen is mixed with the gas, this may be detected by the production of red acid fumes on exposing the gas to the air, or by the dark color imparted to a fresh solution of protosulphate of iron when added to a jar of the gas. If the protoxide is intended for respiration, it is necessary, in the first instance, to test it for these noxious impurities. It may be deprived of any traces of chlorine and deutoxide by passing it through a solution of potassa before collecting it.

Properties.—Protoxide of nitrogen is not a permanently elastic gas. It may be liquefied by great pressure (p. 74). The liquid protoxide mixed with sulphide of carbon produces, by rapid evaporation, the greatest degree of cold yet observed; namely, 220° below the zero of Fahrenheit (p. 74). The gas itself is solidified at about 150° below zero. The cold produced by the evaporation of the liquid protoxide, placed *in vacuo*, is sufficient to solidify it; under atmospheric pressure it evaporates slowly. Liquid mercury sinks in it and is instantly frozen to a solid. A piece of red-hot charcoal will at the same time float on it, and burn brilliantly wherever it touches the liquid. The gas is colorless; it has a slight odor and a sweet taste. It is soluble in water, and this solubility leads to a great loss of the gas when it is allowed to stand in contact with water. Cold water will dissolve about its own volume, but the gas will be again given out on boiling the solution. Its admixture with air may thus be known, as the gas should be entirely removed by its volume of water. It is quite neutral when pure; it neither reddens nor bleaches litmus.

As it contains half its volume of oxygen it possesses some of the properties of that gas, modified, however, by the presence of nitrogen. Thus it supports combustion. A taper burns in it vividly, and is rapidly consumed. Like oxygen, it kindles into flame a glowing wick, a glowing piece of wood or ignited nitre-paper. Sulphide of carbon or ether inflamed on tow, and introduced into this gas, burns with great splendor. In these cases there is a halo of a peculiar reddish color around the flames, arising probably from the combustion or incandescence of nitrogen at a high temperature. Sulphur and phosphorus require to be strongly heated before they will burn in this gas. Iron does not burn in it, and charcoal only glows in it when intensely heated, producing carbonic acid. It differs from oxygen—1st, in its great solubility in water; and 2d, when free from air, in the fact that it produces no red fumes when the deutoxide of nitrogen is added to it. This gas is a narcotic poison, and, when breathed, rapidly destroys the life of an animal. It may, however, be taken by a human being in limited quantity; and if the lungs be emptied before it is inhaled, it rapidly causes a peculiar species of intoxication, manifested at first by unsteadiness of gait, and subsequently by violent muscular exertion. There is a brilliant flow of ideas, with, generally speaking, a great disposition to pugnacity. From the pleasing kind of delirium which it produces it has been called "the laughing or paradise gas." When breathed, it is rapidly absorbed into the blood, and produces a great change in that fluid—manifested by a dark-purple color of the lips, and by a livid or pallid appearance of the face. Some have fallen down at once powerless, but the greater number are thrown into a state of violent excitement, running swiftly from the spot and scattering everything before them. Some dance, others sing, and some make speeches of an incoherent kind, evidently under the impression that they are masters of elocution. An instance is referred to by Sir David Brewster, in which the effects were manifested by an uncommon disposition for pleasantry and mirth, and by extraordinary muscular power, in a person of gloomy mind. The effects continued in a greater or less degree for more than a week. In general the exhilarating effects pass off in from five to ten minutes, and, with the exception of some prostration of strength and slight headache, no injurious symptoms have followed. It is right to state, however, that in certain cases, probably from idiosyncrasy, the respiration of the gas has been attended with severe headache, giddiness, double vision, and even some delirium, with a feeling of weakness from exhaustion lasting for several days. It is not to be regarded as an anæsthetic, like chloroform or ether-vapor. It is a powerful excitant and stimulant to the nervous system.

Composition.—At a full red-heat this gas is decomposed, and two volumes of it are resolved into two volumes of nitrogen and one volume of oxygen, so that it acquires an increase of bulk. The analysis of the gas may be effected by detonation with hydrogen. When a mixture of one volume of the protoxide and one volume of hydrogen is fired by the electric spark, water is produced, and one volume of nitrogen remains ($NO+H=HO+N$). Now, as one volume of hydrogen takes half a volume of oxygen to form water, the protoxide must consist of one volume or equivalent of nitrogen and half a volume or an equivalent of oxygen; these being so condensed, in consequence of chemical union, as only to fill the space of one volume. The decomposition of one volume of the gas, by heating in it the metal potassium, gives the same results. One volume of nitrogen is left as a residue.

	Atoms.	Equiv.	Per cent.	Vol.	Sp.Gr.
Nitrogen	1 =	14	63·6	1·0	0·97
Oxygen	1 =	8	36·4	0·5	0·55
Protoxide of Nitrogen	1	22	100·0	1·0	1·52

The specific gravity and equivalent of this gas are the same as those of carbonic acid. One hundred cubic inches of it weigh 47·08 grains. It is, therefore, half again as heavy as the atmosphere. If a lighted taper be placed at the bottom of a tall jar of air, the gas may be poured into this jar, and the fact that it falls to the bottom, will be indicated by the increased brilliancy in the combustion of the taper. If a tall jar containing the gas, be left uncovered for some time, it will be found, by occasionally introducing a taper with a glowing wick, that this will be kindled into flame, proving that, by reason of its density, the gas still remains there. So if ignited nitre-paper be brought over a jar of the gas, the smoke, instead of suddenly falling through it as through air, will float in the form of a dense cloud on the top of the gas.

This gas enters into no combinations which call for remark. It has been artificially produced by the slow deoxidation of nitric acid, as where one part of nitric acid is diluted with from 12 to 16 parts of water, and some granulated zinc is added to the liquid.

Tests.—The properties already described are sufficient for its identification. It is known from all other gases, excepting oxygen, by its effects on combustible bodies, and from oxygen by the negative action of deutoxide of nitrogen.

Deutoxide of Nitrogen (NO_2).—*Binoxide of Nitrogen. Nitric Oxide. Nitrous Gas.*—This gas was first accurately described by Priestley in 1772. It may be procured by putting some copper-filings or clippings into a gas-bottle with nitric acid diluted with two or three parts of water; the acid is decomposed, red fumes are produced, and there is a copious evolution of the gas, which may be collected and preserved over water. In this mode of obtaining the gas, 3 atoms of copper and 4 of nitric acid produce 3 of nitrate of copper and 1 of nitric oxide, $4NO_5+3Cu=3[CuO,NO_5]+NO_2$. The first portions should be rejected, as containing nitrogen and nitrous acid vapor. The latter being soluble in water is speedily removed.

Properties.—The deutoxide of nitrogen is a colorless, neutral, unliquefiable gas; its specific gravity compared to hydrogen is as 15 to 1. 100 cubic inches weigh 32·10 grains; and, compared with air, its specific gravity is as 1·0365 to 1000. Under common circumstances, it is permanent over water; but if agitated with water previously deprived of air by long boiling, it is dissolved in the proportion of about 1 volume to 20. This solution, when long kept, is found to contain nitrate of ammonia, resulting from the joint decomposition of the deutoxide and the water.

It is rapidly fatal to animals; but as it will always meet with a sufficiency of oxygen in the lungs, to convert a part of it into nitrous acid, the noxious effects observed, may have depended on this acid. When the gas has been well washed with water, it is not acid, a fact which may be proved by the color of litmus remaining unchanged by it. The experiment may be thus performed: After having washed the jar (which should contain no water), and the plate which confines the gas, introduce it into a basin of blue litmus, and withdraw the cover. The gas may thus remain in the litmus without altering the blue color; but when the jar is raised out of the liquid, so as to admit a portion of air, red acid fumes are produced, and upon again plunging it into the litmus, the liquor will be reddened and the acid vapors absorbed. The red fumes which are formed when the gas is exposed to air, are those of nitrous acid ($NO_2+2O=NO_4$). They have a peculiar suffocating odor, and are highly irritating and corrosive. Care should be taken that they are not breathed, even in a diluted state.

The gas extinguishes the flame of a taper, ignited camphor, and sulphur. Phosphorus readily burns in it if introduced in intense ignition; but it is extinguished unless in vivid combustion, and it may be touched with a hot wire in the gas, without taking fire. Boiling phosphorus decomposes the gas, nitrogen is evolved, and phosphoric acid is formed.

If dry nitre-paper is ignited and suddenly plunged into this gas, it will continue to glow, chiefly at the expense of the oxygen of the nitrous acid, produced when the jar is uncovered. It is remarkable that this gas should not support the combustion of a taper, since it contains in equal volumes, as much oxygen as the protoxide, and only half the quantity of nitrogen. If mixed with the protoxide, it will readily support combustion. Potassium and sodium, when heated to ignition in air, burn in this gas with great splendor: sodium burns with a light which rivals that of phosphorus. It is decomposed when passed over charcoal at a red heat—carbonic acid is formed and nitrogen is set free, $NO_2+C=N+CO_2$, but neither charcoal nor sulphur will burn in this gas. If introduced in a state of ignition they are extinguished, but the vapor of sulphide of carbon mixed with the deutoxide and ignited, completely decomposes it with the evolution of the most intense light, and the production of carbonic and sulphurous acid, at the expense of its oxygen, ($3NO_2+CS_2=2SO_2+CO_2+3N$). For the performance of this experiment, we may employ a stout jar, holding 200 cubic inches of deutoxide. About a drachm of the sulphide should be poured into the jar, which should be agitated, in order to promote the diffusion or the vapor before the mixture is ignited.

Deutoxide of nitrogen is not altered by a low red heat, but it is decomposed when passed and repassed through small tubes heated to bright redness, especially if the heated surface is increased by filling the tubes with fragments of rock crystal, or by the introduction of platinum wire. It does not detonate when mixed with two volumes of hydrogen, and subjected to the electric spark; a succession of sparks, however, passed through such a mixture, slowly effects the decomposition of a portion. The pure gas is itself partially decomposed by a succession of sparks into nitric acid and nitrogen. When mixed in equal volumes with hydrogen, and the mixture is kindled, it burns with a greenish-white flame and a reddish-colored halo: but there is no explosion. Water is produced and nitrogen is set free ($NO_2+2H=2HO+N$). When a mixture of 2 volumes of this oxide and 5 of hydrogen are passed through a tube containing spongy platinum, and after the expulsion of the air, the tube is heated, the platinum becomes ignited, and water and ammonia are formed ($NO_2,+5H=NH_3,2HO$). An inflamed jet of hydrogen is extinguished in the gas. Some substances which have a strong attraction for oxygen, effect a partial decomposition of the deutoxide, and convert it, at common temperatures, into the protoxide of nitrogen; such, for instance, as moist iron-filings, some of the alkaline sulphides, some of the sulphites, and protochloride of tin; in these cases two volumes of the deutoxide produce one of the protoxide. Deutoxide of nitrogen may also be decomposed, at high temperatures, by the action of some of the metals which absorb its oxygen. Sir H. Davy decomposed it by heated arsenic and by the ignition of charcoal. (*Elements*, 260.) Gay-Lussac decomposed 100 measures of it by the action of heated potassium: 50 measures of pure nitrogen remained, and the loss of weight corresponded to 50 measures of oxygen; so that two volumes of the gas are resolved into one volume of oxygen and one volume of nitrogen. Similar results have been obtained by passing the gas over copper turnings heated to redness in a tube. The deutoxide then is constituted of one volume of nitrogen and one volume of oxygen, combined without change of volume; and its atomic constitution as well as its specific gravity may be thus represented:—

	Atoms.	Equ.	Per cent.	Vols.	Sp. Gr.
Nitrogen	1	= 14	46·67	1	0·4837
Oxygen	2	= 16	53·33	1	0·5528
Deutoxide	1	= 30	100·00	2	1·0365

Plucker has submitted this gas to spectral analysis, in a quantity so small as to be scarcely recognizable by the most sensitive balance. The red band of nitrogen was obtained in great splendor, and near to it was a bright band derived from the oxygen; but the latter was gradually extinguished. A similar result was obtained with protoxide of nitrogen.

The most characteristic chemical property of this gas, by which it is immediately distinguished from all other gases, is that of forming red fumes, chiefly of nitrous acid vapor, when mixed with air or oxygen ($NO_2+2O=NO_4$); hence these gases are mutually used to detect each other's presence. As nitrous acid is absorbed by water, oxygen may be abstracted from any gaseous mixture containing it by the addition of a sufficient quantity of the deutoxide; and, on the other hand, the deutoxide may be removed by the addition of oxygen.

Solutions of the protochloride and protosulphate of iron dissolve this gas, forming a deep greenish-black liquid, having, in reference to the sulphate, the following composition, $(4FeO,SO_3)+NO_2$. These solutions speedily absorb oxygen when exposed to, or agitated with air, or other mixtures containing it. (*See* page 148.) This property enables us to ascertain the purity of the deutoxide, which ought wholly to be absorbed by the solution of iron: some nitrogen or protoxide is thus generally detected in it, by its remaining unabsorbed. According to Peligot (*Ann. Ch. et Ph.* 54.17,) the proportion of the gas absorbed by protosulphate of iron is definite, and in the ratio of one equivalent to 4 of the protoxide of iron, in accordance with the formula above given. By exposure to a vacuum the gas escapes, and the salt of iron remains unaltered; but when heated, a part only of the gas is evolved, and a part is decomposed, while peroxide of iron and ammonia are formed. When this solution is exposed to air or oxygen, nitric acid is ultimately produced.

When the deutoxide is perfectly dry, chlorine exerts no action upon it, but the presence of water causes an immediate change; it is decomposed, and, furnishing oxygen to the nitric oxide, and hydrogen to the chlorine, hyponitrous and hydrochloric acids are generated. It was the presence of water which misled those who thought that the red fumes produced by mixing deutoxide and chlorine over water, resulted from the existence of oxygen in chlorine. These may, however, arise from the presence of air as impurity in the chlorine.

Tests.—This gas is known by the red acid fumes which it produces when brought in contact with air, and by its entire solubility in a solution of protosulphate of iron.

HYPONITROUS ACID (NO_3).—*Azotous Acid. Nitrous Acid.*—This compound is generally designated by continental chemists, Nitrous acid. Gay-Lussac found by mixing deutoxide of nitrogen and oxygen in tubes standing over mercury, and containing a little concentrated solution of potassa, that 400 volumes of deutoxide were condensed under such circumstances by 100 of oxygen. When, however, he attempted to decompose the hyponitrite of potassa thus obtained, nitric oxide was evolved, and nitrous acid formed. Dulong obtained hyponitrous acid (mixed with nitrous acid) by passing a mixture of 1 measure of oxygen with somewhat more than 4 of deutoxide, first through a tube filled with fragments of porcelain to insure perfect mixture, and afterwards through a bent tube, cooled below 0°. The acid collected in the tube was a dark-green fluid, more volatile than nitrous acid, and when distilled leaving a yellow liquid, which appeared to be nitrous acid. Liebig obtained hyponitrous acid by heating 1 part of starch in 8 of nitric acid, sp. gr. 1·25, and conducting the evolved gases first through a tube filled with fragments of chloride of calcium, and then into a tube cooled down to 0°; a very volatile liquid was thus condensed, colorless at 10°, but green at common temperatures. According to Fritzsche, hyponitrous acid may be obtained by gradually adding, by means of a tube drawn out to a fine point, 45 parts of water (5 atoms) to 92 parts of nitrous acid (2 atoms) cooled down to 0°, and distilling into a receiver, surrounded by a freezing mixture, until the boiling-point rises to 82°. The product is of an indigo-blue color. Its vapor is orange-colored, and its boiling point below 82°; but when distilled, it is partially decomposed into deutoxide and nitrous acid. It is very doubtful whether, by any of these processes, the acid has been yet obtained in an absolutely pure state. It appears to be generally mixed with nitrous or nitric acid. Its instability is so great, that it is decomposed by water ($3NO_3=NO_5+2NO_2$) into nitric acid and deutoxide. It is better known in combination with bases, and its composition has been determined by the analysis of its compound with silver. It consists of:—

	Atoms.	Equiv.		Volumes.		Volumes.
Nitrogen . . .	1 ...	14 ...	36·8	1 or 2	=	Deutoxide 4
Oxygen . . .	3 ...	24 ...	63·2	1½ or 3		Oxygen 1
Hyponitrous acid .	1	38	100·0			

Hyponitrites (Nitrites).—When nitrate of potassa, or nitrate of baryta is strongly heated, the acid loses two atoms of oxygen, and a hyponitrite of the base is formed: $KO,NO_5=KO,NO_3+2O$. When properly prepared, a small portion of the fused residue, will give a dense white precipitate, with a solution of nitrate of silver. If the salt has been overheated, the precipitate will be brown. *Hyponitrite of potassa* thus obtained, is a white deliquescent salt, very soluble in water and alcohol. By its solubility in alcohol, it may be separated from any undecomposed nitrate. The white precipitate which it produces with nitrate of silver, is soluble in nitric acid as well as in a large quantity of water. It may be obtained in crystals from a hot saturated solution. By double decomposition with the chloride of any alkaline metal, other hyponitrites may be obtained. It is impossible to procure hyponitrous acid in a free state from these salts. When an acid is added to a hyponitrite, deutoxide of nitrogen escapes, and a nitrate is formed ($3KO,NO_3+2SO_3=$

KO,NO_5+2NO_2+2KO,SO_3). If an acid solution of a hyponitrite is warmed, it becomes a powerful deoxidizer; thus it discharges the pink color of the permanganate of potassa, peroxide of manganese being formed. From a solution of chloride of gold, the metal is precipitated; the color of a solution of indigo is discharged by it, and a solution of protosulphate of iron acquires a deep greenish-black color. The hyponitrites are thus easily distinguished from the nitrates, by the action of acids, and by their reducing agency on solutions of gold and permanganate of potassa. Some of the hyponitrites may be produced by the action of deutoxide of nitrogen on the respective alkaline liquids. Thus when this gas is kept for some weeks in contact with a strong solution of potassa, it is converted into protoxide, and the potassa-solution yields on evaporation a hyponitrite ($2NO_2+KO=KO,NO_3+NO$). It was this reaction which led Gay-Lussac to the discovery of the acid. 100 volumes of deutoxide left 25 of protoxide: the acid, therefore, which was absorbed, consisted of 100 volumes of nitrogen and 150 of oxygen. According to Berzelius, several of the hyponitrites are best obtained by boiling metallic lead in a solution of nitrate of lead, by which a *hyponitrite of lead* is formed: this salt may then be decomposed by sulphates, which form sulphate of lead, and the hyponitrous acid unites to the base of the original sulphate. Mitscherlich prepares the hyponitrites by the mutual action of soluble chlorides and hyponitrite of silver. (*See* SILVER.)

NITROUS ACID (NO_4).—*Hyponitric Acid. Hypoazotic Acid. Peroxide of Nitrogen.*—When 2 volumes of deutoxide of nitrogen and 1 volume of oxygen, dried by potash, are mixed in an exhausted glass vessel, the gases combine with the evolution of heat consequent upon their mutual condensation, and form *nitrous acid vapor*, which is condensable into a nearly colorless liquid at 0°, and crystallizes at a somewhat lower temperature. The specific gravity of this liquid is 1·45; at 32° it is of a pale yellow color; but at 60° deep orange: it boils at 82° (Gay-Lussac); and when exposed to the air at common temperature, gradually evaporates in orange-red fumes. When a mixture of the gases, in the above proportions, is propelled through a tube cooled to 20°, the liquid acid is at once obtained; but at 16° it crystallizes in prisms. If the gases be mixed over water, hyponitrous acid and nitric acid are formed at low temperatures, ($2NO_4=NO_3+NO_5$); and at higher temperatures nitric acid and deutoxide are the results ($3NO_4=2NO_5+NO_2$). The product of the distillation of dry nitrate of lead appears to be nitrous acid, nearly, if not quite, pure and anhydrous ($PbO,NO_5=NO_4+PbO+O$). The powdered nitrate, previously well dried, should be put into a small retort, with the beak drawn out, and introduced into a small tube receiver, which should be immersed in a freezing mixture. A strong heat is required for the distillation, and when a sufficient quantity of the liquid acid has been collected, the tube may be sealed by applying the flame of a spirit-lamp to the elongated neck. It can only be preserved in sealed tubes.

Properties.—Nitric acid *vapor* supports the combustion of phosphorus and of charcoal, but extinguishes burning sulphur. These experiments may be performed on the vapor procured by passing a jet of oxygen into a jar, or bell-glass, filled with deutoxide of nitrogen, until the mixture acquires an orange-red color. A lighted taper, as well as ignited nitre-paper, glow in this vapor, and continue to burn. The oxidizing properties of the acid vapor, and its power of destroying foul effluvia, may be shown by inverting over a jar of it, another containing sulphuretted hydrogen gas. The sulphur is separated with evolution of great heat ($NO_4+2HS=NO_2+2HO+2S$). A solution of iodide of potassium is instantly decomposed by it, and the iodine set free. A diluted solution of permanganate of potassa has its pink color discharged by it as a result of deoxidation.

Its color, like that of the liquid acid, varies with the temperature, becoming darker when heated, and paler when cooled; it has a peculiar suffocating odor, which strongly adheres to the hair and to woollen clothing. The anhydrous *liquid* has no acid properties, and does not apparently unite with bases, but forms with them *hyponitrites* and *nitrates* ($2NO_4+2KO=KO,NO_5+KO,NO_3$); hence it has been regarded as a peroxide of nitrogen, or a compound of hyponitrous and nitric acids ($2NO_4=NO_3+NO_5$). When passed over baryta or other bases, at a temperature of between 300° and 400°, it is rapidly absorbed with the evolution of heat, and the products are a nitrate and a hyponitrite. (GAY-LUSSAC, *Ann. Ch. et Ph.* 1.)

Nitrous acid vapor is constituted of 1 volume of nitrogen, and 2 volumes of oxygen, condensed into 2 volumes, or, as above stated, 2 volumes of nitric oxide, and 1 volume of oxygen ($NO_2+2O=NO_4$). Its specific gravity, therefore, to hydrogen, will be as 46 to 1; to air, as 1·589 to 1. It is actually found to be 1·7. It is constituted of:—

	Atoms.	Equ.	Per cent.	Vols.	Sp. Gr.
Nitrogen	1	14	30·4	0·5	0·4837
Oxygen	4	32	69·6	1·0	1·1057
Nitrous acid	1	46	100.0	1·	1·5894

Nitrous acid is not decomposed by a red heat, but it is a powerful oxidizer, and parts with its oxygen readily to sulphur, phosphorus, and the metals. When the acid vapor is passed over metallic copper heated to redness, it gives up its oxygen, and nitrogen escapes. By this process, its composition has been accurately determined. The acid is decomposed by water, when this liquid is in large proportion, nitric acid being dissolved and deutoxide of nitrogen escaping ($3NO_4+2HO=NO_2+NO_5,HO$). When the quantity of water is small, although the same products result, the nitric acid holds the nitrous acid dissolved, and acquires, according to its specific gravity, a variety of colors. Nitric acid of a high specific gravity appears to be the proper solvent of this compound. Thus when saturated with it, nitric acid of a specific gravity of 1·510 is of a deep orange color, at 1·410 (*aquafortis* of commerce), yellow, at 1·320 greenish-blue, at 1·150 colorless. In the latter case, the quantity of water is so great as to decompose the nitrous acid in solution, and to transform it into colorless nitric acid.

Although this acid does not combine directly with alkaline bases, it forms a series of remarkable compounds with organic bases. M. Martin's researches have shown that the varieties of gun-cotton, or pyroxyline, are compounds of nitrous (hyponitric) acid, with this substance as a base. The fulminating compound contains 5 equivalents of the acid, while the photographic cotton contains 4. The compound with 3 equivalents of the acid is of a pulverulent nature, and when dissolved in alcoholic ether, leaves an opaline residue on evaporation; while another compound with 2 equivalents of acid is known by its solubility in water. (*Cosmos*, Juin 28, 1861, p. 769.) The large amount of oxygen contained in this acid, accounts for the great combustibility of the first of these compounds.

NITRIC ACID (NO_5).—*Azotic Acid*, and in its monohydrated state, HO,NO_5, or H,NO_6. The composition of this acid was first demonstrated by Cavendish, in 1785. He produced it by passing a succession of electric sparks through a mixture of 7 volumes of oxygen and 3 of nitrogen. This result has been verified by Faraday (*Experimental Researches*, 3d series, § 324), in reference to the appearance of minute quantities of nitric acid in the rain of thunderstorms. Nitric acid is also formed when deutoxide of nitrogen is slowly added to an excess of oxygen gas, over water. In this way 4 volumes of deutoxide of nitrogen are condensed, and they combine with 3 volumes of oxygen.

Anhydrous Nitric Acid (NO_5) was discovered by Deville, in 1849.—(*Ann. Ch. et Ph.*, 3me Sér. vol. 28, p. 241.) He obtained it by passing dry chlorine over dry nitrate of silver, placed in a U-tube, and heated to 303°, which temperature is lowered, as soon as the action commences, to between 136° and 154°. The products are chloride of silver, oxygen, and anhydrous nitric acid ($AgO,NO_5+Cl=NO_5+AgCl+O$). Some nitrous acid is at first evolved, but at the lower temperature, crystalline anhydrous nitric acid is separated, and may be condensed in a second tube, surrounded by ice. There are many precautions requisite to insure the success of the operation; no organic matter, such as cork, &c., should be used in the apparatus.

Anhydrous nitric acid crystallizes in colorless rhombic prisms. The crystals fuse at about 85°: and the liquid boils and is decomposed at 113°. They dissolve in water, producing great heat, but no gas is disengaged. The crystals, like those of other anhydrous acids, have no acid reaction until dissolved (*see* page 41). They are liable to be decomposed with explosion at the common temperature, being suddenly converted into oxygen and nitrous acid.

Hydrated Nitric Acid.—*Preparation.*—(HO,NO_5) is usually obtained by the distillation of purified *nitre* with sulphuric acid. The nitric acid of commerce, which is generally red and fuming, in consequence of the presence of nitrous acid, is procured by the distillation of 2 parts of nitre with 1 of sulphuric acid; these proportions yield about 1 part of orange-colored nitric acid of the specific gravity of 1·48. Some manufacturers employ 3 parts of nitre and 2 sulphuric acid, and the *London Pharmacopœia* directs equal weights, by which nearly a colorless nitric acid is afforded, provided the distillation is conducted at as low a temperature as possible. Nitrate of soda being cheaper than nitrate of potash, is frequently resorted to as a source of nitric acid. As nitre generally contains a little sea salt, the first portions of acids which come over are impure, containing chlorine and nitrous acid, but they serve to wash quite clean the neck of the retort, on which some sulphuric acid is commonly to be found, in spite of all our care, as well as traces of powdered nitre; it is best, therefore, to collect the first portion, say one-tenth of the whole, in a separate receiver, and when the liquid that drops is found to be free from chlorine (by the test of nitrate of silver), the receiver may be changed, and the rest of the nitric acid obtained quite pure, or, at most, slightly tinged by nitrous acid. When 2 equivalents of sulphuric acid (oil of vitriol) to 1 of nitre are used, the results are 1 equivalent of hydrated bisulphate of potassa and 1 of monohydrated nitric acid; $KO,NO_5+2[HO,SO_3]=KO,HO,2SO_3+HO,NO_5$. When 100 parts of nitre, 96·8 of oil of vitriol, and 40·45 of water are mixed and distilled, at 266° to 270°, nitric acid, of specific gravity 1·4, passes over during the whole process. (Mitscherlich.)

Oil of vitriol of the sp. gr. 1·84, contains one equivalent of dry sulphuric acid and *one* of water; whereas liquid nitric acid usually contains one equivalent of dry acid and *two* of water: hence the requisite excess of oil of vitriol, where colorless and perfect nitric acid is to be obtained; hence, too, the red color of the acid of commerce, in consequence of the smaller quantity of oil of vitriol generally used by the manufacturer, the deficiency of water causing the nitric acid to be resolved into nitrous acid and oxygen.

The nitric acid, or aquafortis of commerce, is always impure, and hydrochloric and sulphuric acids may generally be found in it. The former may be detected by nitrate of silver, and the latter by a diluted solution of nitrate of baryta. If, however, pure nitre and pure sulphuric acid be employed in its production, and the latter not in excess, there is little apprehension of impurity in the resulting acid. If the acid is colored by the presence of nitrous acid, it is rendered colorless by boiling, which is best performed in a retort, with a loosely-attached receiver; the nitrous acid passes off. If it contain hydrochloric acid, this is also decomposed by boiling, and chlorine escapes. Iron may generally be detected in the common acid by the usual test, ferrocyanide of potassium. The acid should be diluted and neutralized before applying the test. If pure, nitric acid should leave no residue on evaporation.

Properties.—Pure nitric acid is a colorless liquid, very acid and corrosive, acting powerfully upon organic substances. Its specific gravity, as usually obtained, fluctuates between 1·4 and 1·5. At 247°, when of the specific gravity 1·42, it boils and distils over as a hydrate $(NO_5,4HO)$, without change, but the diluted acid is strengthened by boiling; and the strongest acid boils at a lower temperature (184°) than that which is of a lower specific gravity.

At —40° the concentrated acid is congealed. When diluted with half its weight of water, it freezes at about —2°. When the acid of 1·45 is exposed to the air, it exhales fumes of a peculiar odor, and gradually absorbs water, so that its bulk becomes increased, and its specific gravity diminished. It suffers a partial decomposition when exposed to light, becoming yellow and evolving oxygen, so that it should be kept in a dark place, and especially excluded from the direct rays of the sun (NO_4+O). Nitric acid, of the sp. gr. 1·5, mixed with half its bulk of water, occasions an elevation of temperature in the mixture=112°: 58 parts of the acid with 42 of water, both at 60°, give, on mixture, a temperature of 140°. On diluting the red fuming acid, it assumes a green color—the tint depending upon the quantity of water added.

Anhydrous nitric acid is a compound of—

	Atoms.	Equ.	Per cent.	(Deville.)
Nitrogen	1	14	25·9	25.4
Oxygen	5	40	74·1	74·6
	1	54	100·0	100·0

The liquid nitric acid in its utmost state of concentration (sp. gr. 1·520) consists of 1 equivalent of anhydrous acid and 1 of water. It is a monohydrate. According to Dr. Ure, the acid of a specific gravity of 1·486 contains 1 equivalent of real acid and 2 of water:—

	Sp. gr. = 1·520.			Sp. gr. = 1·50.			Sp. gr. = 1·486.			Sp. gr. = 1·424.		
Anhydrous acid	1	54	85·72	1	54	80	1	54	75	1	54	60
Water . .	1	9	14.28	1½	13·5	20	2	18	25	4	36	40
	1	63	100·00	1	67·5	100	1	72	100	1	90	100

The following table, drawn up by Dr. Ure, exhibits the quantity of dry acid in 100 parts at different densities (*Quarterly Journal*, 4, 297), the quantity of anhydrous acid in the liquid acid of sp. gr. 1·50 being assumed= 79·7. The column of dry acid shows the weight which any salifiable base would gain by uniting so as to form an anhydrous salt, with 100 parts of the liquid acid of the corresponding specific gravity.

Specific gravity.	Dry acid in 100.	Specific gravity.	Dry acid in 100.	Specific gravity.	Dry acid in 100.	Specific gravity.	Dry acid in 100.
1·5000	79·700	1·4228	60·572	1·3056	41·444	1·1587	22·316
1·4790	73·324	1·3882	54·196	1·2583	35·068	1·1109	15·940
1·4530	76·948	1·3477	47·820	1·2084	28·692	1·0651	9·564

Nitric acid may be decomposed by passing its vapor through a red-hot porcelain tube; oxygen is given off, nitrous acid vapor is produced, and a quantity of diluted acid which has escaped decomposition, passes over into the receiver; it is thus proved to consist of nitrous acid, oxygen, and water. At a white heat, oxygen, nitrogen, and water only are evolved. According to Faraday, nitric acid does not undergo electro-chemical decomposition, but the water only. The oxygen at the anode is always a primary result, but the products at the cathode are often secondary, and due to the reaction of the hydrogen upon the acid. (*Phil. Trans.* 1834, p. 96.)

When deutoxide of nitrogen is agitated with concentrated nitric acid, the acid is decomposed, and nitrous acid is formed, partly by the acquisition of oxygen by the oxide, and partly by its loss by the acid ($NO_2+2NO_5=3NO_4$). Hyponitrous acid may also result ($NO_2+NO_5=NO_3+NO_4$). Various colors are thus imparted to nitric acid, according to its density (*see* page 160). If to a jar holding about 150 cubic inches of deutoxide, an ounce of strong colorless nitric acid is added, this undergoes an immediate decomposition. Dense orange fumes fill the jar, and the liquid acquires a deep green or brown color. Nitric acid is so frequently a mixture of the two acids, that it has been proposed to call it the *Acidum nitrico nitrosum* (NO_5HO,NO_4).

Some of the metals, such as copper, tin, and silver, are at first without action on concentrated nitric acid, but become vehemently active upon the addition of a little water. Poured upon hot iron-filings, or melted bismuth, zinc, or tin, nitric acid causes a combustion of the metals. In acting upon those metals which decompose water, nitric acid gives rise to the formation of ammonia, and nitrate of ammonia may be found by the appropriate tests among the products. No ammonia is formed during the action of nitric acid on copper, lead, antimony, bismuth, mercury, or silver. These metals remove three-fifths of the oxygen, the deutoxide of nitrogen being evolved. If the acid is much diluted, zinc and iron take four-fifths, and protoxide of nitrogen is a product. Tin, which is without action on the concentrated acid, deoxidizes it completely when of lower strength, nitrous acid, deutoxide of nitrogen, and nitrogen being set free. Nitric acid is without action on gold and platinum. This enables a chemist to detect the common alloys, which are intended to imitate gold, as nitric acid immediately dissolve them with the evolution of deutoxide of nitrogen. It is hence called the jeweller's test. But gold may be alloyed with nine per cent. of copper, and the acid will not affect it. The action of protosulphate of iron upon this acid is somewhat remarkable. If a strong solution of the protosulphate be added to a small quantity of nitric acid, the liquid acquires a dark, greenish-black color. The nitric acid parts with three-fifths of its oxygen, and the deutoxide of nitrogen which results, is dissolved by the sulphate (*see* page 157). The reaction of the oxide of iron upon the acid may be thus represented, $6FeO+NO_5=NO_2+3Fe_2O_3$. The dark liquid has the composition $4(FeO, SO_3)+NO_2$.

The facility with which nitric acid imparts oxygen, renders it a valuable oxidizing agent. Phosphorus decomposes it at common temperatures, and sulphur and carbon when aided by heat. A piece of glowing charcoal thrown upon the surface of the concentrated acid, burns vehemently with the evolution of red fumes. It acts energetically (often when diluted) upon the greater number of organic bodies, and mutual decompositions ensue. A drachm of oil of turpentine, mixed with half a drachm of sulphuric acid, instantly bursts into flame upon the addition of a drachm of nitric acid. Malic, oxalic, and carbonic acids are the common products of the action of diluted nitric acid, upon many vegetable and animal substances; ammonia and hydrocyanic acid are also sometimes formed. It tinges many animal substances of a yellow color, and permanently stains the nails and skin; it is sometimes employed in the production of yellow patterns upon woollen goods. Its oxidizing powers are increased by the presence of nitrous acid (NO_4). Pure nitric acid has no action on a solution of permanganate of potassa, but if it contain nitrous or hyponitrous acid, the red color of the solution is discharged.

Tests.—*Nitrates.*—Nitric acid is monobasic. There are no acid nitrates; the salts are neutral, and are represented by the formula $MO+NO_5$. Among the metals, there are, however, some basic salts. As the salts of nitric acid are all soluble in water, neither its presence nor its proportion can be determined by precipitation. When uncombined, it is recognized: 1. By its action on copper, and the production of deutoxide of nitrogen. 2. By the solution of gold when mixed with boiling hydrochloric acid. 3. By its discharging the color of sulphate of indigo acidulated with sulphuric acid when the mixture is heated.

Nitric acid, when neutralized by potassa, yields long striated prisms of nitrate of potassa, and when neutralized by soda, rhombs. Other tests for this acid are included in those which are required for the detection of a *nitrate.* 1. On adding sulphuric acid to a nitrate, colorless fumes of nitric acid are given off. 2. On performing this experiment in a small test-tube, and adding a few copper-filings, nitrous acid fumes are evolved, known by their odor, their orange-red color, acidity, and the decomposition of a mixture of iodide of potassium and starch. When the quantity of nitrate is small, this experiment should be performed in a Florence flask—starch paper wetted with a solution of the iodide of potassium being suspended in the neck of the flask, which should be corked. 3. Add to the nitrate, dissolved in a small quantity of water, its volume of sulphuric acid, and when nearly cool, add a crystal of protosulphate of iron. The crystal is encircled with a pink or brownish-colored layer of liquid (*see* page 157). 4. On boiling the nitrate with a small quantity of hydrochloric acid and a fragment of leaf-gold, the metal is speedily dissolved. If the gold does not entirely disappear, the fact that some portion has been dissolved, will be manifested by the liquid acquiring a purple or dark color on the addition of a few drops of protochloride of tin. The copper test may fail to reveal the presence of a nitrate when an alkaline chloride is present. In this case, the gold-test will be found serviceable. The nitrates are frequently present in potable waters, and their presence is generally indicative of the infiltration of nitrogenous matters, and their subsequent oxidation. They may be easily detected, without separating the other salts, by the application of the gold-test to the residue left on evaporation. 5. A solution of a nitrate, tinted blue with sulphate of indigo, acidulated with sulphuric acid, and heated, causes a destruction of the color.

CHAPTER XIV.

COMPOUNDS OF NITROGEN AND HYDROGEN. AMMONIA AND ITS SALTS.

It is generally conceded by chemists that there are three compounds of these elements—*Amidogen*, NH_2; *Ammonia*, NH_3; and *Ammonium*, NH_4; Of these, only one has been isolated, namely, *ammonia*, a gaseous alkali; and as the two hypothetical compounds are derived from it, it is this which will first claim attention.

AMMONIA ($NH_3=17$).—This is a compound alkaline gas, long known under the name of volatile alkali. It derives its name from the temple of Jupiter Ammon, in Libya, in the neighborhood of which sal ammoniac was at one time manfactured. This gas is found in the atmosphere in very small proportion.

Preparation.—When nitrogen and hydrogen are mixed in the free state, they show no tendency to combine; they diffuse without change, and each is separable from the other. It is only in the *nascent* state that they combine to form ammonia (*see* page 44). This gaseous compound may be obtained from a mixture of equal parts of dry quicklime and one of dry hydrochlorate of ammonia, finely powdered, introduced into a small retort, and gently heated. It must be collected over mercury. Towards the latter part of the operation, a little water goes over, which may be arrested in the neck of the retort by the previous introduction of a piece of blotting-paper, or of stick potassa, or it may be prevented passing over by filling up the bulb of the retort with powdered lime. Hydrochlorate of ammonia is a compound of hydrochloric acid and ammonia; by the action of the lime (which is an oxide of calcium) the ammonia is expelled in its pure and gaseous form: the hydrochloric acid and the lime then mutually decompose each other, and water and chloride of calcium are the results: $CaO,+NH_3,HCl=CaCl,+HO+NH_3$. The gas may likewise be procured by heating in a retort, a saturated solution of ammonia.

Properties.—Ammonia is gaseous at common temperatures, but it may be liquefied by a cold of —40°, or at the temperature of 40° by a pressure of 6·5 atmospheres (Faraday, *Phil. Trans.*, 1823, p. 196). It is most readily obtained as a liquid by disengaging it by heat, in a sealed tube, from chloride of silver which has been previously saturated with the gas (page 73). It forms a colorless transparent liquid, of a specific gravity of 0·76, and with a refractive power surpassing that of water. When free from water, it does not conduct electricity. At 103° below 0°, this liquefied ammonia became a white, translucent, crystalline solid, heavier than the liquid.

Gaseous ammonia has a pungent and suffocating odor: it irritates the nose, eyes, and throat, and is irrespirable; but when diluted by mixture with common air it is an agreeable stimulant. It converts some vegetable blues to green, yellows to red, and reds to blue or green, properties which belong to the bodies called *alkalies.* Ammonia, therefore, has been termed *volatile alkali*, and the change of color thus effected by it is distinguished from that produced by the fixed alkalies by the return of the original tint when the paper is warmed, or after the ammonia has passed off by exposure. Dry ammonia has no action on dry vegetable colors (page 45). (Kane.) As it is collected in the state of gas, it always holds sufficient water to act upon vegetable colors. If a small jar of the gas is opened under a large receiver, in which are suspended strips of paper colored with tincture of turmeric, infusion of roses, a decoction of Brazil wood, and litmus reddened by an acid, these will speedily undergo the changes of color which are characteristic of an alkali. Paper stained with the yellow sulphide of arsenic is bleached in the gas, while that which is wetted with arsenio-nitrate of silver (mixed solutions of arsenious acid and nitrate of silver) acquires a yellow color. It combines with the acids, and produces an important class of salts.

The specific gravity of ammonia, compared with hydrogen, is as 8·5 to 1; compared with air it as 0·5873 to 1; 100 cubic inches weigh 18·19 grains. The gas extinguishes flame, but it is partially burned with a yellow flame, which does not extend to the other portions of the gas. Owing to its lightness, this experiment may be performed in a jar inverted. When mixed with air, it may be burned as it issues from a capillary orifice in an atmosphere of oxygen. When mixed with its volume of oxygen it burns with a feeble explosion. Ammonia is abundantly absorbed by chloride of calcium, as well as by several other chlorides (chloride of silver), with which, and with the other haloids, it forms compounds. Hence if it be required artificially to dry the gas, potassa or lime should be used.

Water, at the temperature of 50°, takes up 670 times its volume of ammonia, its bulk is increased (6 measures of water giving 10 of the solution), and its specific gravity is diminished; that of a saturated solution is 0·875, water being 1·000. A saturated solution of ammonia readily floats on water. The following table shows the quantity of ammonia in solutions of different specific gravities (Davy, *Chem. Phil.*, p. 268):—

100 parts of Sp. gr.		Of Ammonia.	100 parts of Sp. gr.		Of Ammonia.
·8750	contain	32·50	·9435	contain	14·53
·9000	"	26·00	·9513	"	12·40
·9166	"	22·07	·9573	"	10·82
·9326	"	17·52	·9692	"	9·50

The solutions of this gas commonly met with are the three following:—

	Saturated solu.	Common.	P. L.
S. G.	·875	·889	·960
Ammonia . . .	32.3	26	10
Water	67·5	74	90
	100·	100·	100·

The solubility of the gas in water may be shown by the following experiment. Fill a tube with dry ammonia, and invert it in a basin containing a small quantity of mercury. Pour into the basin a solution of litmus just reddened by tartaric acid. Raise the tube containing the ammonia, so that the mouth may be immersed in the colored liquid. The liquid will gradually rise in the tube, and will ultimately fill it if the gas is pure. At the same time the alkaline nature of the gas will be proved by the red liquid being turned blue. A lighted taper applied to a small jar of the gas is extinguished. If a little water be added, and the jar shaken, the solution of the gas will be proved by the taper now burning in the jar.

The great solubility of ammonia in water renders it easy to separate this gas from many others which are insoluble in this liquid. The usual state in which ammonia is employed is in aqueous solution, both in chemistry and medicine. This solution (*Liquor Ammoniæ*) may be readily obtained by passing the gas into water in a proper apparatus, or by distilling over the water and gas together. For this process equal parts of sal-ammoniac and well-burned quicklime may be employed: the lime is slaked by the addition of water, and, as soon as it has fallen into powder, placed in an earthen pan, and covered until quite cold, then mixed with the powdered sal-ammoniac and put into a proper retort, and heated as long as it gives out gas, which should be conducted, by means of a safety-tube, into a quantity of distilled water, equal to the weight of the salt employed. The specific gravity of a solution of ammonia so obtained is ·936.

Liquid ammonia (as this aqueous solution is sometimes called) should be preserved in well-stoppered glass bottles, since it loses ammonia and absorbs carbonic acid when exposed to air. The gas is constantly evolved, and, when the solution is heated, ammonia is rapidly given off by it; when concentrated, it requires to be cooled to —40° before it congeals, and then it is inodorous, and of a gelatinous appearance. If a piece of ice be introduced into a jar of gaseous ammonia standing over mercury, it melts with great rapidity, and liquid ammonia is produced. This is owing to the strong affinity of this gas for water.

The solution, when pure, is colorless, and has the pungent odor of the gas. It is strongly alkaline, irritant, and caustic. It differs from potassa and soda in redissolving the oxides of copper and silver, precipitated by alkalies from their solutions. It should leave no residue on evaporation. If it contains carbonic acid, this may be detected by the addition of lime-water, or a solution of chloride of calcium, either of which will then cause a white precipitate of carbonate of lime. The presence of chlorine may be detected by neutralizing the alkaline solution with nitric acid, concentrating it by evaporation, and then adding nitrate of silver. The presence of chlorine is made evident by the appearance of an insoluble white precipitate of chloride of silver.

Tests.—Ammonia as a gas is recognized by its odor and volatile reaction, as well as by its producing white fumes of hydrochlorate of ammonia, when a rod dipped in strong hydrochloric acid, is brought near to it. Its solution is precipitated, 1st, by a solution of tartaric acid, when added in large proportion (acid tartrate of ammonia); and 2d, by a solution of chloride of platinum, forming a pale yellow ammonio-chloride of that metal, which is insoluble in alcohol. When existing in solution in very minute proportion, and the absence of other alkalies has been proved by the entire evaporation of a portion of the liquid, traces of ammonia may be readily detected by adding a few drops of the mixed solutions of arsenious acid and nitrate of silver. Yellow arsenite of silver is produced and precipitated. The solution of ammonia is an important agent to the chemist. It enables him to precipitate many bodies, and as it is volatile, it can be subsequently expelled by heat from any mixture to which it has been added.

Composition.—Dr. Henry first observed that a mixture of ammonia and oxygen might be fired by an electric spark, and this property furnishes a method of analyzing the gas. When the spark-current from Ruhmkorff's induction-coil, is discharged through ammonia, the gas is rapidly decomposed, and at the same time the liberated gases evolve the light peculiar to nitrogen and hydrogen. The spectrum produced, results from the superposition of the spectra for hydrogen and nitrogen. When a succession of electric sparks has been passed through a quantity of the gas contained in a tube over mercury, it is uniformly observed to increase to twice its original volume, and at the same time to lose its alkalinity and solubility in water. If the gas thus expanded, is mixed with from one-third to one-half of its bulk of oxygen, and an electric spark passed through the mixture, an explosion takes place, attended by a considerable diminution of volume. Assuming that in the analysis 4 c. i. of ammonia are expanded to 8 c. i. by the electric spark, and that 3 c. i. of oxygen are mixed with the 8 c. i. of decomposed gas, there will be 11 c. i. of mixed gases. These after detonation are reduced to 2 c. i., water being produced by the oxygen combining with the hydrogen of the decomposed ammonia. Two-thirds of the loss, or 6 c. i., represent hydrogen (*Water*, page 117), and the 2 c. i. of residuary gas may be proved to be nitrogen. Hence ammonia is constituted of one volume or atom of nitrogen, and three volumes or atoms of hydrogen, the four volumes being reduced by combination to two. The changes are represented in the following equation: $2NH_3+6O=2N+6HO$. This method of analysis is open to the objection that some nitrogen is converted by the electric spark to nitric acid, which may lead to error in computing the loss after detonation. The following plan is not attended with this difficulty. Let 100 c. i. of the gas be passed through a porcelain tube containing platinum-wire heated to redness; it will be doubled in volume and entirely decomposed. The 100 c. i. of ammonia produce 200 c. i. of mixed gases, of which 50 are nitrogen and 150 may be proved to be hydrogen.

These results are confirmed by ascertaining the sp. gr. of the gas; but as the atom of ammonia represents two volumes, the sum of the sp. gr. of the constituents must be divided by 2. Thus:—

Specific gravity of nitrogen . . . . . = 0·9674
" hydrogen. . 0·0691 × 3 = 0·2073

1·1747÷2=.5873

Ammonia, therefore, is a compound of

	Atoms.		Weights.		Per cent.		Vols.
Nitrogen	1	...	14	...	82·35	...	1
Hydrogen	3	...	3	...	17·65	...	3
Ammonia	1		17		100·00		2

Ammonia is produced synthetically during the decomposition of many animal and vegetable substances, or by simply heating nitrogenous matter; it is also formed during the action of nitric acid upon some of the metals; and by moistened iron-filings exposed to an atmosphere of nitrogen or air. In these cases the nascent gases unite so as to form a portion of ammonia ($Fe_2+4HO+N=Fe_2O_3,HO+NH_3$). Rust of iron formed by the exposure of iron to a damp atmosphere, generally contains traces of ammonia. When nitric acid is added to a mixture of zinc and dilute sulphuric acid, its nitrogen combines with the hydrogen as it is evolved, and ammonia is formed, $NO_5+8H=NH_3+5HO$; when, however, the action is violent, some deutoxide of nitrogen is also evolved. If, after some days, a portion of the liquid is boiled with a solution of potassa, ammonia will be evolved. The production of this gas during the rusting of iron may be thus proved. Sprinkle the inside of a large stoppered bottle with fine iron-filings, adding a small quantity of water to make the metallic particles adhere to the sides of the bottle. Suspend in the interior from the stopper a slip of litmus-paper, first reddened by a weak acid. In about twenty-four hours the paper will be rendered blue, by the ammonia produced in the rusting of iron. In the action of nitric acid upon tin, ammonia is a product, provided water is present. Add tin-filings to nitric acid, and then dilute the acid until a violent action commences. The acid and the water are partially deoxidized by the metal, and the hydrogen of the one unites to the nitrogen of the other, in the nascent state, to form ammonia ($NO_5+3HO+4Sn=NH_3+4SnO_2$). If the residuary oxide of tin be well mixed with water, and some lime stirred into the mixture, ammonia is immediately evolved. Ammonia, as it is diffused in air and water, is liable to become oxidized and converted to nitric acid, as a result of the action of ordinary or allotropic oxygen, $NH_3+8O(Oz)=NO_5+3HO$. This oxidation is chiefly observed to occur when fixed bases, with which the acids can combine, are present. The presence of alkaline nitrates in large quantity in many well-waters, especially in the neighborhood of grave-yards, is attributed to the effects of oxidation on the ammoniacal products of putrefaction.

Ammonia may be synthetically formed by the action of spongy platinum on a mixture of 2 volumes of deutoxide of nitrogen and 5 of hydrogen. For such experiments platinated asbestos, formed by dipping that substance into a solution of chloride of platinum and exposing it to a red heat, may be used; while the mixed gases are passing, the platinum should be heated ($NO_2+H_5=NH_3+2HO$.)

AMIDOGEN (NH_2).—Amidogen is presumed to exist in combination with certain metals, and in some organic compounds. When potassium, or sodium, is heated in a current of dry ammonia, one equivalent of hydrogen is expelled, and a solid substance is obtained which, in the case of potassium, is supposed to have the composition KNH_2—an atom of hydrogen having been replaced by an atom of the metal. This theory is strongly supported by the fact, that when the substance produced is placed in water, the sole products obtained are potassa and ammonia, $KNH_2+HO=KO+NH_3$. Amidogen is therefore regarded as a hypothetical radical. Among the compounds into which it is supposed to enter, may be mentioned those of copper, $CuNH_2$, and mercury, Hg,NH_2, the last being the ammonio-chloride of mercury or white precipitate. Inferring from these and other similar cases, that in ammonia the third atom of hydrogen is less intimately combined with nitrogen than the remaining two, Sir Robert Kane represents amidogen, NH_2 by the symbol Ad, and treats it as the radical of ammonia. Ammonia, therefore, on this view of its constitution, is an *amide of hydrogen*$=NH_2,H$ or AdH.

AMMONIUM ($NH+_3H$, or NH_4).—When mercury is made the negative electrode in an aqueous solution of ammonia, it becomes semi-solid, and assumes the character of a soft amalgam; oxygen is given off at the positive electrode, but there is no corresponding evolution of hydrogen on the negative side until the electric current is interrupted, when the metallic sponge begins to collapse, and gives out hydrogen and ammonia, leaving a residue of pure mercury; but this change may be retarded by cold, and on cooling the pasty mass to 0° it yields cubic crystals, which, when decomposed over mercury, give out ammonia and hydrogen in the respective volumes of 2 to 1. The mercury, therefore, appears to have been combined with a body represented by NH_4, and as the metallic characters of the mercury are unchanged, it is presumed that NH_4 constitutes temporarily a metal which has been termed *ammonium.* This phenomenon may be equally observed by placing an amalgam of potassium or sodium and mercury upon a block of sal ammoniac, excavated in the form of a cup and containing a small quantity of water; the amalgam soon increases in size, and forms a soft solid. It is supposed, in this case, that the potassium-amalgam, acting upon hydrochlorate of ammonia, gives rise to chloride of potassium, and the amalgam of ammonium, $KHg+NH_3HCl=KCl+HgNH_4$. The production of this amalgam may be more strikingly shown by the following experiments. Prepare an amalgam of sodium by gently warming some mercury in a tube or capsule, and adding at intervals, small portions of sodium. The amalgam, which should be fluid when cold, may be preserved for some hours in a well-stoppered bottle. Prepare a few ounces of saturated solution of chloride of ammonium. Fill a tall glass or jar to about one-third with this solution at the temperature of 100°, then pour into it a quantity of the prepared sodium-amalgam. On contact with the liquid, the amalgam rapidly enlarges into a spongy mass, sometimes rising out of the glass and forming a cauliflower excrescence. If kept in contact with the solution, it retains its spongy state for a short time; but the mass slowly collapses: hydrogen and ammonia are evolved, and metallic mercury remains in the glass, which now contains a solution of the chlorides of ammonium and sodium.

In the production of the *ammonium-amalgam* while the metal increases to ten times its volume in the cold and probably to thirty times its volume at 100°, the hydrogen and ammonia increases its weight, only by 1·2000th part. When a portion of the amalgam is placed in water tinted with red litmus, it is slowly decomposed, minute bubbles of hydrogen escape, and the solution of the ammonia is proved by the red litmus slowly acquiring a blue color. The evolution of these gases may be further proved by filling a long test-tube to two-thirds of its depth, with blue infusion of cabbage, and the other third with ether. If the amalgam is dropped to the bottom of the tube, the ammonia, as it escapes, will be dissolved by the water, and turn the blue cabbage green, while the hydrogen not being soluble will be seen escaping in numerous minute bubbles through the floating layer of colorless ether.

These facts simply show that hydrogen and ammonia go into the mercury, and that they are again evolved as such either spontaneously or by contact with water. Although not isolated in a combined state, it is assumed—1, from the consistency given to the mercury; 2, from the amalgam crystallizing in cubes at zero, that the hydrogen and ammonia are temporarily united in definite proportions, to form a metal which is dissolved by mercury like other metals. At temperatures above zero the tendency of the components of this metal to assume the elastic state appears to be so great as to lead to their evolution under the form of hydrogen and ammonia. It is remarkable that in the analysis and synthesis of this body the elements are never arranged as hydrogen and nitrogen, but as hydrogen and ammonia.

Although this compound metal cannot be separated as such from the amalgam, chemists have generally agreed to regard its independent existence as sufficiently established to justify its use in the nomenclature of the salts of ammonia, thereby assimilating them in some respects to the salts of the other alkaline metals. The hypothetical ammonium is, therefore, symbolized sometimes as Am, or more commonly by the formula NH_4. The salts will stand thus upon the two theories:—

	Potassium series.	Ammonium series.		Ammonia series.
Metal	K	Am	$= NH_4$	$NH_3 + H$
Oxide	KO	Am,O	$= NH_4O$	NH_3,HO
Chloride	KCl	AmCl	$= NH_4Cl$	NH_3,HCl
Sulphide	KS	AmS	$= NH_4S$	NH_3,HS
Nitrate	KO,NO_5	AmO,NO_5	$= NH_4\,O,NO_5$	NH_3,HO,NO_5
Sulphate	KO,SO_3	AmO,SO_3	$= NH_4\,O,SO_3$	NH_2,HO,SO_3

From this comparative table it appears, that while potassium is an alkaligenous metal, *i. e.*, a metal producing an alkali by combination with oxygen, ammonia is a metalligenous alkali, *i. e.*, an alkali producing a metal, by combination with hydrogen. While oxide of potassium (KO) is an independent and well-defined compound, which can be readily obtained either with or without water, the so-called oxide of ammonium has only a hypothetical existence. Dry ammonia, like dry potassa, has no alkaline reaction, the presence of water being required for the manifestation of this property in bodies (p. 41). There is, however, no reason to suppose that the water is decomposed by either compound. In reference to ammonia, water acts simply as a solvent, as it does on carbonic acid and protoxide of nitrogen. The properties of the solution are simply those of the gas, and like other soluble gases, ammonia may be entirely expelled by heat. There is no hydrate of ammonia, nor any condition of this alkali, which shows a chemical union with or reaction upon the elements of water. Every attempt to extract an oxide has ended in failure, and even where circumstances were most favorable for its production—*i. e.*, in the nascent state—nothing but ammonia and water result.

When perfectly *dry* ammonia and hydrochloric acid gases are brought in contact—a solid white crystalline salt is formed, which may be either hydrochlorate of ammonia, or chloride of ammonium. On the latter hypothesis, the affinity of the ammonia for another equivalent of hydrogen is assumed to be such as to lead to its separation from the chlorine ($NH_3+HCl=NH_4,Cl$). But the production of this binary compound is not reconcilable with the facts usually observed in reference to the powerful affinity of chlorine for hydrogen. Ammonia itself is readily deprived of all its hydrogen by chlorine, as in one of the processes for obtaining nitrogen ($NH_3+3Cl=N+3HCl$). In reference to the extraction of ammonia by lime, most chemists treat sal-ammoniac as hydrochlorate of ammonia, and not as chloride of ammonium. On the former view there is simply a displacement of the ammonia by the lime, and the production of water, $NH_3,HCl+CaO=NH_3+CaCl+HO$; on the latter view, the decomposition would be, $NH_4,Cl+CaO=NH_3+CaCl+HO$. Thus synthetically, the ammonia is supposed to be changed into a metal by a reaction on the elements of hydrochloric acid; while analytically, the metal is supposed to be reconverted into ammonia and water by a reaction on the constituents of lime. It will be perceived that the oxacid salts of ammonia enumerated in the table contain an atom of water, and this is supposed to furnish the hydrogen for the production of the metal, and the oxygen necessary to constitute its oxide.

While the alkaline metals manifest no basic properties until after they have entered into combination with oxygen, ammonia, in a dry state, forms saline compounds with dry sulphurous and carbonic acids, and even with the anhydrous sulphuric, and phosphoric acids. These compounds have received the name of *Ammonides*, to distinguish them from the salts formed with the hydrated oxacids. Ammonia must therefore be regarded as exceptional in this respect. The production of a metal, or of the oxide of a metal, is not necessary for the manifestation of basic properties by this alkali.

SALTS OF AMMONIA.—*Nitrate*, NH_3,HO,NO_5.—It is usually obtained by saturating pure nitric acid with carbonate of ammonia, evaporating and crystallizing.

This salt was formerly called *nitrum flammans*, in consequence of its rapid decomposition with a slight explosion when heated to about 600°. At 228° it enters into perfect fusion; at 356° it boils without decomposition; at about 390° to 400° it is decomposed, and is entirely resolved into protoxide of nitrogen and water ($NH_3HO,NO_5=2NO+4HO$). It is deliquescent, and soluble in less than its weight of water at 60°. Its taste is acrid and bitter. It indicates free acid after exposure to air, and, like other ammoniacal salts, it loses its neutrality and becomes acid when its solution has been boiled.

Hydrochlorate of Ammonia; Muriate of Ammonia, NH_3HCl; *Chloride of Ammonium*, NH_4Cl.—This salt may be produced directly, by mixing equal volumes of dry gaseous ammonia and dry hydrochloric acid, when entire condensation ensues. The experiment which beautifully illustrates the solidification of two gases by chemical union, may be thus performed. Place within a tall, stoppered shade, a small jar containing ammonia. When the gas has diffused itself, which may be known by a change of color in test-paper placed at the top of the shade—the stopper may be removed, and a small jar of hydrochloric acid inverted over the aperture. A dense white cloud of chloride of ammonium will immediately descend from the top to the bottom of the shade. Under the name of *sal-ammoniac* this salt was formerly imported from Egypt, where it was obtained by burning the dung of camels. It is now prepared either by saturating hydrochloric acid with carbonate of ammonia, or by decomposing sulphate of ammonia by chloride of sodium ($NH_3,SO_3,HO+NaCl=NH_3,HCl+NaO,SO_3$). When obtained by evaporation from its solution in water, it forms octahedral crystals; but, in commerce, it usually occurs, as procured by sublimation, in translucent fibrous cakes, hard, somewhat elastic, and slightly deliquescent. In this compact state it requires for solution about an equal weight of water at 212°, and nearly three times its weight at 60°, cold being produced during its solution. It is also sparingly soluble in alcohol. When heated it sublimes, before it fuses, without decomposition, in the form of a white vapor, and may be even passed through a red-hot porcelain tube without change.

Sal-ammoniac is an anhydrous salt; it is not volatile at common temperatures, but when exposed to air it becomes slightly acid, in consequence of the loss of a little ammonia; the aqueous solution, therefore, of the salt, often reddens litmus. It is used in the arts for a variety of purposes, especially in certain metallurgic operations; it is used in tinning, to prevent the oxidation of the surface of copper; it is also employed in small quantities by dyers.

Sesquicarbonate of Ammonia, $2NH_3,3CO_2,2HO$.—This salt is the carbonate of ammonia of commerce. It is generally met with in translucent cakes of a fibrous fracture, as obtained by sublimation from a mixture of carbonate of lime and sulphate or hydrochlorate of ammonia. When carbonate of lime and sulphate of ammonia are used for its production, the results are sulphate of lime, hydrated sesquicarbonate of ammonia, and free ammonia and water. $3[CaO,CO_2]+3[NH_3,SO_3,HO]=3[CaO,SO_3]+[2NH_3,3CO_2,2HO]+NH_3,HO$. When sal-ammoniac is substituted for the sulphate, we have $3[CaO,CO_2]+3[NH_3,HCl]=3CaCl+[2NH_3,3CO_2,2HO]+NH_3,HO$.

This salt has a pungent odor, a hot and saline taste, and a powerful alkaline reaction. It may be obtained in an impure state by the destructive distillation of nitrogenous matter, constituting *salt of hartshorn*; but this and other salts of ammonia, are now chiefly procured from the distillation of coal, in the manufacture of gas. Four parts of water at 60° dissolve about one of this salt, forming the *liquor ammoniæ sesquicarbonatis*. When exposed to air, especially in the state of powder, it effloresces into bicarbonate of ammonia, and carbonate of ammonia is volatilized. When its aqueous solution is heated, carbonic acid and a little ammonia is evolved, and the single carbonate remains dissolved. There is a *bicarbonate* of ammonia (NH_32CO_22HO) on the ammonia theory; but to satisfy the ammonium hypothesis, this must be regarded as a carbonate of ammonia and carbonate of basic water $[HO,CO_2+NH_4O,CO_2]$. This difficulty applies to all the acid salts of ammonia.

Characters of the Salts of Ammonia.—They are white, soluble in water, and are volatilized when heated. With the exception of the carbonate, they have no odor of ammonia. The solutions are rendered acid by boiling. In the dry state, a salt of ammonia is known by heating it in powder with its bulk of quicklime, and in a state of concentrated *solution*, by boiling it with a solution of potassa. *Ammonia*, recognizable by its odor and other properties, is evolved in both cases.

For *Sulphide of Ammonium*, see Hydrosulphuric acid.

CHAPTER XV.

CHLORINE (Cl=36).—COMPOUNDS WITH OXYGEN AND HYDROGEN. HYDROCHLORIC ACID.

History.—CHLORINE is an elementary gas, which was discovered by Scheele in 1774. For a long time it was supposed, on the authority of Lavoisier, to be a compound of oxygen and muriatic acid, and it was thence called *Oxymuriatic acid gas*; but in the year 1810 it was examined by Davy, and proved by him to be a simple undecomposable body of highly negative properties, like oxygen. It derives its name, chlorine, from its greenish-yellow color (χλωρὸς, green). The alleged presence of oxygen and muriatic acid in the gas, was explained by its reaction under the influence of light, on the elements of water—the gas having been examined in the humid state. Under these circumstances the hydrogen was taken by the chlorine forming hydrochloric acid and the oxygen was evolved. It is not found free in nature; its combining tendencies are so strong, that it could not long exist in the free state. It is a most abundant element, and is the great constituent of the sea, as oxygen is of the earth. It is hence called a *halogen* (ἅλς, salt). One pound of common salt (chloride of sodium) contains more than half a pound of chlorine. This is equivalent to rather more than five gallons of the gas, for each gallon of sea-water.

Preparation.—Chlorine may be procured by acting on a mixture of sea salt and black oxide of manganese with sulphuric acid; but it will be found more convenient to obtain it directly from hydrochloric acid, which contains 97 per cent. of this gas. The peroxide of manganese, in coarse powder, is mixed with four parts, by weight, of hydrochloric acid, to which a little water is added to check the fumes. A flask or retort may be used, but two-thirds of the capacity of the vessel should be left free, as the mixture swells up when heated. By the application of a gentle heat the gas will come over freely. It should be collected in a bath containing but a small quantity of tepid water. It is very soluble in water, and much is lost by collecting it in cold water. If hot water is used there is less of the chlorine dissolved, but on cooling, the gas is liable to become mixed with a large proportion of air. It must not be allowed to stand over water, or it will entirely disappear. The jars should stand on accurately fitted glass-plates, and the vessels which are not ground may be placed in plates containing a small quantity of a saturated solution of chlorine. The decomposition which ensues in the above-mentioned process, may be thus represented: $2HCl+MnO_2=Cl+MnCl+2HO$. From this it will be perceived, that only one-half of the chlorine is obtained. It may be procured from common salt by heating a mixture of four parts of chloride of sodium, and one part of peroxide of manganese, with two of sulphuric acid and two of water ($NaCl+MnO_2+2SO_3HO=NaO,SO_3+MnO,SO_3+Cl+2HO$).

The gas may be procured quite pure and dry, by passing it first through a wash-bottle containing some distilled water, and afterwards through a glass-tube containing broken chloride of calcium. As the respiration of even a small quantity of chlorine is highly injurious to the lungs, the gas should be made only where there is a free current of air. The first portions (containing air) should be collected in jars, and these may be opened under a flue. The gas should not be collected for experiments, until it appears of a rich greenish-yellow color. As it is very heavy, it may be obtained by displacement. For this purpose the gas, dried by the process above described, should be conducted by a delivery-tube to the bottom of a clean dry jar, and when the colored gas is seen to overflow, the jar may be covered and removed. For common purposes, chlorine may be speedily dried by placing some strong sulphuric acid at the bottom of the jar in which it is to be collected, and causing the delivery-tube to dip into this. The chlorine in passing through the sulphuric acid is deprived of its water, and if the jar, when filled, is closely covered, and is allowed to stand for a short time, the gas will be perfectly desiccated.

Properties.—Chlorine gas is of a greenish-yellow color, has a pungent and suffocating odor, a peculiar and somewhat astringent taste, is highly irritating when respired, exciting cough and great irritation of the lungs, even when considerably diluted with atmospheric air. When dry and pure, it is not affected by light, neither is it altered by a high temperature. But when the gas in a humid state is passed through a red-hot porcelain tube, it decomposes the watery vapor, combining with the hydrogen to form hydrochloric acid, and liberates oxygen. Although a gas at the ordinary temperature and pressure, chlorine admits of liquefaction by cooling to —106°, or by a pressure of four atmospheres at 60°, forming a yellow liquid which has not been yet solidified. Chlorine readily combines with aqueous vapor to form a crystalline hydrate of a pale yellowish-green color. A jar of the gas containing the ordinary amount of vapor, readily yields this hydrate when exposed to a temperature of 32°. If the temperature rises, the crystals melt, and the jar will be again filled with the gas, which is set free with effervescence. This hydrate of chlorine consists of one atom of the gas to ten atoms of water ($Cl+10HO$); it may be obtained in a pure state, by placing a small quantity of water in a large bottle containing chlorine, and keeping the bottle in a dark place at or near the freezing point. If these crystals are introduced into a small bent tube, and the tube is sealed, they will serve as a source for obtaining the gas in the liquefied state (*see* page 73). On heating the end containing the crystals, and keeping the other end of the tube cool, a yellow vapor is evolved which is condensed into two distinct fluids, the upper and lighter being an aqueous solution of chlorine, while the lower and heavier, which is of a yellow color, is the liquefied gas. When the tube is broken, the liquid is immediately converted to gaseous chlorine. The sp. gr. of the liquid gas is 1·33. It is a non-conductor of electricity.

The specific gravity of chlorine compared with air is 2·4876, which gives 77·04 grains as the weight of 100 cubic inches at mean temperature and pressure. Its specific gravity, in reference to hydrogen, may be considered as 36 to 1. In the electrolysis of its compounds, chlorine, like oxygen, appears at the positive pole or anode.

At the temperature of 60°, water dissolves twice its volume of the gas. The solution, saturated at 42°, has a specific gravity of 1·003; it is of a pale greenish-yellow color, has an astringent, nauseous taste, and destroys vegetable colors: hence its use in bleaching. The bleaching agency has been by some regarded as due to the evolution of nascent oxygen, resulting from the decomposition of aqueous vapor or water. Chlorine itself, when perfectly free from moisture, has no such action. Thus if a strip of dry litmus-paper be placed in a jar of chlorine collected by displacement through sulphuric acid in the manner already described, it will be found that that portion of the paper which is in the jar retains its blue color, while that which hangs out of the jar will be bleached. The mouth of the jar should be closely covered by a plate of glass, or the moisture in the air will cause a bleaching of the whole of the litmus-paper. The general effect of the humid gas on organic colors may be thus represented ($Cl+HO=HCl+O$). Indigo, litmus, cochineal, aniline-purple, and other colors, are thus so completely destroyed, that they cannot be artificially restored.

The bleaching properties of the gas may be shown by passing a few cubic inches of it into a jar filled with diluted sulphate of indigo, and inverted in the water-bath. The color of the indigo is destroyed on agitation. Let some artificial flowers and a bunch of parsley be suspended in a tall shade filled with water and inverted in the bath. On decanting into the shade chlorine gas, so as to fill the upper part of it, the colors depending on organic compounds will be destroyed, while mineral colors, including those depending on carbon, will remain.

The *aqueous solution* of chlorine was formerly known as oxymuriatic acid. It is now called *aqua chlorinata*. It has no acid reaction, unless it has been exposed to light. It is a powerful astringent, and possesses all the bleaching and oxidizing properties of the gas. It converts sulphurous into sulphuric acid ($Cl+SO_2+2HO=HCl+SO_3HO$), and the protoxides of iron and manganese into peroxides. The ferrocyanide of potassium is changed to ferricyanide by chlorine. This solution gives a white precipitate with nitrate of silver ($AgCl$), insoluble in nitric acid. When exposed to a temperature of 32°, the aqueous solution freezes, forming the crystalline hydrate (page 174), and ice which is free from chlorine. The aqueous solution of chlorine dissolves gold by the aid of a gentle heat. When this solution is exposed to the direct rays of the sun, oxygen is evolved in consequence of the decomposition of the water, the hydrogen of which unites to the chlorine, and forms hydrochloric acid ($Cl+HO=HCl+O$). The same change ensues more slowly in common daylight, but in the dark, there is no such decomposition; so that as gaseous chlorine generally contains aqueous vapor, the bottles in which it is preserved, should be carefully excluded from light.

Chlorine, and its aqueous solution, are powerful antiseptics, and destroyers of foul and noxious effluvia. This property depends on its power of decomposing the noxious compounds, which generally contain hydrogen, and resolving them into others which are harmless. For the purposes of fumigation, chlorine liberated at common temperatures, from black oxide of manganese and hydrochloric acid, or from manganese, salt, and sulphuric acid, may be diffused through the foul atmosphere. In the same way the offensive odor of decomposing animal matter, may be removed by sprinkling it with a solution of chlorine.

When a burning taper is immersed in a jar of this gas, the flame becomes red, throws off dense, black fumes, and is soon extinguished. If a green wax taper with a glowing wick is suddenly introduced into a jar of the gas, the flame will be rekindled, and it will continue to burn with the evolution of much carbonaceous smoke. Tow or cotton, impregnated with ether, and introduced in a state of flame into the gas, burns with a dense smoke, chiefly of carbon. Bibulous paper soaked in hot oil of turpentine suddenly plunged into a jar of the gas (kept partially covered) frequently bursts into flame, a large quantity of carbon being given off during the combustion. In all these cases, chlorine supports combustion, by taking only the hydrogen of the combustible, and setting free the carbon. That hydrochloric acid is a product, may be proved by introducing litmus-paper, which will be reddened —as well as a glass rod dipped in strong ammonia, which will cause the evolution of copious white fumes of hydrochlorate of ammonia. Some bodies—such as sulphide of carbon, which burn with great splendor in oxygen—are immediately extinguished in this gas. There are, however, many substances, such as phosphorus and several of the metals, which are spontaneously inflamed by chlorine, and burn in it with much energy. Phosphorus burns in the gas at all temperatures (*see* page 97). In these cases, binary compounds result, some of which, like those of oxygen, are possessed of acid properties: others are not acid, and are termed *chlorides.* Brass or copper leaf, and powdered antimony, serve well to show the intense action of chlorine upon certain metals. When introduced into the gas, they enter into immediate combustion, and chloride of copper and chloride of antimony are formed.

Fill a dry jar with some leaves of Dutch gold, and invert over it a jar of pure chlorine; as the gas descends, the metal will undergo combustion, acquiring a red heat without flame, and the whole will disappear. The combustion of antimony may be shown by sifting the freshly-powdered metal into a jar of the gas on partially removing the cover. If a piece of sodium, heated to ignition in air, be introduced into a bell-jar of the gas, it will burn with great splendor. If a coil of fine iron-wire is made red hot and plunged into the gas, it will burn with a deep lurid-red flame, evolving copious brown vapors of sesquichloride of iron. When fine copper or brass wire ignited is employed, it burns in chlorine with splendid scintillations. Arsenic and mercury at a high temperature burn in the gas, producing highly noxious fumes. These experiments should only be performed where there is a free current of air to carry off the volatile products.

Chlorine displaces bromine and iodine from their metallic and non-metallic combinations. Paper wetted with a solution of bromide of potassium, and introduced into chlorine, acquires a yellow color from the liberated bromine. If iodide of potassium is used, iodine is abundantly set free.

There is no body for which chlorine manifests so strong an affinity as for hydrogen. All the hydrogen compounds of carbon, sulphur, phosphorus, nitrogen, antimony, and arsenic, are decomposed by it: hydrochloric acid is produced, and the metal or metalloid is liberated. If a jar of chlorine is inverted over one containing sulphuretted hydrogen, this gas is decomposed, sulphur is precipitated, and hydrochloric acid is formed. This may serve as an illustration of its operation in deodorizing foul and offensive effluvia. The decomposition of ammonia by this gas has been already referred to. The whole of the hydrogen is taken and the nitrogen is liberated ($3Cl+4NH_3=3(NH_3HCl+N)$) (page 170). The results may be shown in another mode. Introduce into a jar of chlorine bibulous paper saturated with a strong solution of ammonia. There is violent combustion with a pale reddish flame (chloride of nitrogen ?), and dense white fumes of hydrochlorate of ammonia escape ($6Cl+4NH_3=3(NH_3HCl)+NCl_3$). Ammonia may be regarded as the most effectual agent for the removal or neutralization of gaseous chlorine. Solutions of potassa and soda absorb the gas, producing salts which vary according to circumstances. A current of the gas passed into a hot and concentrated solution of potassa, produces chloride of potassium and chlorate of potassa, which may be obtained by evaporation ($6KO+6Cl=5KCl+KOClO_5$). If the alkaline solution is cold and much diluted, then a chloride and hypochlorite are produced. (See *Hypochlorous Acid.*)

Equivalent and Compounds.—The atomic weight of chlorine is usually taken at 36 (page 61), and its combining volume 1. Like hydrogen, it is a monatomic gas. Its range of combination is as great as that of oxygen. It combines with all the metals, and with the greater number of metalloids. These binary compounds are called *Chlorides.* It forms only acid compounds with oxygen and hydrogen.

Tests.—The color, odor, and bleaching properties of this gas are in all cases sufficient for its identification. In *solution* it may be known by these properties, and by the white curdy precipitate which it gives with a solution of nitrate of silver, as well as by its power of decomposing iodide of potassium, and producing a deep-blue-colored compound when the iodide is mixed with a solution of starch. An excess of chlorine destroys this color.

COMPOUNDS OF CHLORINE AND OXYGEN.—These elementary bodies do not combine directly. They have but a feeble affinity for each other, and, when combined, are readily separated by slight causes. There are five compounds of these elements, four of which are acids:—

1 Hypochlorous acid, ClO
2. Chlorous acid, ClO_3
3. Peroxide of Chlorine, ClO_4
4. Chloric acid, ClO_5
5. Perchloric acid, ClO_7.

1. *Hypochlorous Acid* ($ClO=44$). When a small quantity of hydrate of lime is placed in a jar of chlorine, the gas soon disappears, and a compound of hypochlorite of lime and chloride of calcium is formed ($2CaO+2Cl=CaO,ClO+CaCl$). This is well known as bleaching powder (*see* CHLORIDE OF LIME). When a current of chlorine is passed into a cold weak solu-

tion of soda or potassa, a similar reaction takes place, and an alkaline hypochlorite is formed ($2KO+2Cl=KO,ClO+KCl$). When these compounds are acted upon by acids, they evolve chlorine, and not hypochlorous acid. Balard first suggested a method of obtaining pure hypochlorous acid. His process consists in agitating a mixture of one part of precipitated red oxide of mercury with twelve of distilled water, in a bottle filled with chlorine; the gas is rapidly absorbed. If the proportion of the oxide is insufficient, the deposited powder is white, and some of the chlorine remains unabsorbed; but the oxide should be in slight excess, so as to remain red, and entirely absorb the gas. ($2HgO+2Cl=ClO+HgCl,HgO$.)—(6 drachms of red oxide mixed in fine powder with an ounce and a half of water, and shaken in a quart bottle of chlorine, are the proportions recommended by Graham). When the absorption is complete, the contents of the bottle are poured upon a filter, and the filtered liquor subjected to distillation *in vacuo*, by which a diluted solution of hypochlorous acid is obtained, and this may be concentrated by a second distillation.

The gaseous, is obtained from the aqueous acid, by introducing into an inverted jar of mercury, a quantity of the concentrated liquid, and then passing into it, through the mercury, small fragments of fused nitrate of lime. The nitrate abstracts the water and liberates pure *hypochlorous acid* in the state of a gas, a little deeper-colored than chlorine, of a strong penetrating odor, and absorbable by mercury, forming oxychloride, from the contact of which it is preserved in the above mode of obtaining it, by the layer of solution of nitrate of lime. A slight elevation of temperature, even the warmth of the hand, is sufficient to decompose this gas with explosion and evolution of heat and light, so that it requires careful management. It is not changed by some hours' exposure to diffused daylight, but direct solar rays decompose it in a few minutes without explosion; when mixed with hydrogen and inflamed, it detonates violently, but at common temperatures, the mixture remains unchanged. Bromine and iodine slowly decompose it; sulphur, selenium, phosphorus, arsenic, and antimony, decompose it with sudden and violent detonation; charcoal also causes it to explode, apparently in consequence of the condensation which the gas suffers in its pores. In these cases the elements are peroxidized and converted into the higher class of acids. When placed in contact with iron filings, the iron is oxidized, and chlorine is evolved; but when silver is substituted for iron, chloride of silver is formed, and oxygen is evolved. Hypochlorous acid gas may be procured by passing a current of dry chlorine through precipitated and well-dried oxide of mercury. The gas must be condensed in a receiver, kept cool by a freezing mixture. In this reaction, the oxygen is simply displaced by the chlorine ($HgO+2Cl=ClO+HgCl$), and corrosive sublimate as well as hypochlorous acid results. In performing this experiment, unless the temperature is kept low, oxygen only will be liberated. The gas is formed of a volume of chlorine united to half a volume of oxygen, these being condensed into one volume of the compound. The specific gravity of the gas is in accordance with this constitution; for one half volume of oxygen$=0{\cdot}5528+2{\cdot}4876$ sp. gr. of chlorine$=3{\cdot}0404$. Its specific gravity is, therefore, 3·04, and 100 c. i. weigh 94·16 grains.

According to Regnault, water dissolves at least two hundred times its volume of this gas, forming a pale yellow-colored liquid. The solution possesses powerfully bleaching properties; twice as great in proportion as those of chlorine. This is probably owing to the nascent oxygen which is evolved in its decomposition. It is decomposed by the non-metallic substances, which act upon the gas, and is a most powerful oxidizing agent. It will even oxidize the chloride of potassium, and convert it to chlorate of potassa.

It throws down peroxide of lead from a solution of the chloride of that metal, and sesquioxide of manganese from the chloride. A solution of chlorine produces these effects only under the agency of light. (Regnault.) Chloride of silver exerts upon it a catalytic action, resolving it into its elements without undergoing any change. A concentrated solution of the gas is decomposed by hydrochloric acid, and chlorine is evolved ($HCl+ClO=HO=2Cl$). If the liquids are mixed at a low temperature, a solid crystalline hydrate of chlorine is obtained.

2. *Chlorous Acid* ($ClO_3=60$).—This is a gaseous acid of a greenish-yellow color, not easily liquefied by cold. It may be procured by mixing 3 parts of arsenious acid with 4 parts of chlorate of potassa and sufficient water to make a paste, and adding to the mixture in a retort 12 parts of nitric acid diluted with 4 parts of water. This mixture, distilled in a water-bath, yields a greenish-yellow colored gas (chlorous acid) of a specific gravity of 2·646. (Regnault.) Water dissolves five or six times its volume: the solution has a golden-yellow color. The chloric acid is deoxidized by the arsenious acid, which is converted during the process into arsenic acid. The gas can be collected only in the dry way, as it is very soluble in water, and is decomposed by mercury. It is converted by explosion into chlorine and oxygen at about 130°. Like hypochlorous acid, it oxidizes with explosion, many of the non-metallic bodies. It is a powerful bleaching agent, and is a monobasic acid, forming *chlorites* with bases. The specific gravity of the gaseous acid shows that it must contain in each volume one volume of oxygen and two-thirds of a volume of chlorine—$1·1057+1·6584=2·764$, which does not widely differ from the specific gravity actually determined. In reference to its constitution by volume, it is usually considered that two volumes of chlorine (two atoms), and three volumes of oxygen (six atoms), are condensed into three volumes or atoms of the compound.

3. *Peroxide of Chlorine* ($ClO_4=68$).—This compound, which is sometimes called hypochloric acid, was discovered by Davy, in 1815. It may be procured by acting on fused chlorate of potassa by concentrated sulphuric acid, in the proportion of one part of the salt to three parts of acid. The materials in small quantity may be heated in a tube-retort by a water-bath, at a temperature not exceeding 100°. The gas is soluble in water, which will take up twenty times its volume; and it is decomposed by mercury, hence it can be collected only by displacement. The gas is of a yellowish color, and has a peculiar odor resembling chlorine; it is not acid in reaction, but it has strong bleaching properties. It is decomposed with explosion at about 140°. Phosphorus produces with it violent combustion even under water. This experiment may be performed by placing the powdered chlorate in a tall conical glass with a small quantity of phosphorus, and covering the mixture with cold water. On pouring concentrated sulphuric acid into the mixture by a long funnel the peroxide is set free, and the phosphorus burns with bright scintillations, producing phosphoric acid. The gas may be readily liquefied by cold and pressure. Although not acid, it is dissolved by alkaline liquids, but it forms no saline combinations: on evaporating the alkaline solution, a chlorite and chlorate of the alkali are obtained ($2ClO_4=ClO_3+ClO_5$). The specific gravity of the gas is 2·33. This nearly corresponds to half a volume of chlorine and one volume of oxygen in each volume ($1·2438+1·1057=2·3495$), or in two volumes there would be one volume of chlorine and two volumes of oxygen.

4. Chloric Acid ($ClO_5=76$).—This acid was discovered by Gay-Lussac (*Ann. de Chim.*, xci. 108). It cannot exist independently of an atom of water, or of some base, so that it has not been obtained anhydrous; the hydrated acid, in its state of extreme concentration, being $HO,ClO_5=85$.

In depriving it of water it is converted into peroxide of chlorine and oxygen. Hydrated chloric acid may be prepared by adding diluted sulphuric acid to a solution of chlorate of baryta, as long as it occasions a precipitate. The baryta is thus separated in the form of an insoluble sulphate, and the chloric acid remains in aqueous solution. Care must be taken to add no more sulphuric acid than is requisite, for any excess contaminates the chloric acid. If the exact proportion has been used, the chloric acid is neither rendered turbid by diluted sulphuric acid nor by chlorate of baryta. If either of these occasions a precipitate, the solution must be carefully added till the effect ceases; the clear liquid may then be decanted or filtered off. It may be concentrated by evaporation *in vacuo* until it acquires a syrupy consistency. It may also be procured by the action of fluosilicic acid on chlorate of potassa. A hot aqueous solution of chlorate of potassa is mixed with excess of fluosilicic acid; the acid liquid, when cold, is filtered, evaporated below 80°, and, after two days, filtered through powdered glass.

Hydrated chloric acid is a sour liquid, and of a yellowish tint when highly concentrated. It deoxidizes permanganate of potassa and destroys its color. It reddens vegetable blues, and then bleaches them. When added to a strong solution of potassa, crystals of chlorate of potassa are deposited. When concentrated, it acts powerfully, and even to ignition, upon paper, cotton, and some other dry organic bodies; it decomposes alcohol, with the formation of acetic acid. The most remarkable of its salts, which are now termed chlorates, were formerly known under the name of oxymuriates, or hyperoxymuriates. When distilled at a higher temperature than 100°, it suffers decomposition, and a portion of chlorine and oxygen are liberated, perchloric acid passing over, but no chloric acid. It is decomposed by hydrochloric acid into chlorine and water, $5HCl + ClO_5 = 5HO + 6Cl$. This mixture dissolves gold, and is sometimes employed for the oxidation and destruction of organic matter in toxicological researches. By excess of sulphurous acid, it produces sulphuric and hydrochloric acids; $6SO_2 + ClO_5,HO = 6SO_3 + HCl$: and by excess of sulphuretted hydrogen it forms water, hydrochloric acid, and sulphur; $6HS + ClO_5 = 5HO, + HCl + 6S$. Those acids which are already saturated with oxygen, do not act upon it.

Chlorates.—These salts are $MO + ClO_5$ They deflagrate powerfully with combustible matter, and often by mere friction. (*See* CHLORATE OF POTASSA.) They are all soluble in water. By heat they are mostly resolved into chlorides and evolve oxygen. The electrolysis of the chlorate, when in igneous fusion, has been found by M. Gérardin to present an exception to the general results of the decomposition of salts by current electricity. Thus, in reference to the salts of potassa and soda, in igneous fusion, it was observed that the oxygen only was set free at the positive pole, the radicals of both acid and base appearing at the negative pole. In thus decomposing the fused chlorate of potassa, however, it was found that the oxygen and chlorine appeared at the positive pole in a state of mixture, and the potassium at the negative. This apparent anomaly is probably due to the simultaneous decomposition of the chloride of potassium produced by the effect of heat on the chlorate (*Cosmos*, Oct. 25, 1861, p. 471.)

A chlorate is easily identified by adding to a small portion in powder a drop of sulphuric acid. The odor of peroxide of chlorine is immediately perceived. If a grain or two of white sugar be added to the mixture, there will be immediate combustion. A solution of a *chlorate* colored with indigo has the color discharged in the cold, by the addition of sulphurous acid. When indigo is mixed with the solution of a nitrate, and sulphurous acid is added, the color is not discharged until the mixture has been heated.

The *euchlorine* of Davy, which was produced by the reaction of hydrochloric acid on chlorate of potassa, was probably a compound of chlorous acid and chlorine.

5. PERCHLORIC ACID, ClO_7, or as hydrate$=HO,ClO_7$, was discovered by Count Stadion. It is unknown in the anhydrous state, but it may be procured as hydrate by distilling perchlorate of potassa with its own weight of sulphuric acid, diluted with about a fourth part of water. At a temperature of about 280°, white vapors pass off, which condense in the form of a colorless liquid.

Another method consists in decomposing a hot solution of chlorate of potassa with fluosilicic acid, concentrating the chloric acid by boiling, and subsequently distilling the residue. Dr. Roscoe found that one atom of perchlorate of potassa, distilled with four atoms of concentrated sulphuric acid, also yielded the concentrated hydrate. It is considered to be a more stable compound than the preceding, as it is not decomposed by sulphuric or hydrochloric acid. When concentrated, its specific gravity is 1·6, and it boils at 392°. By distillation with strong sulphuric acid, it may be obtained in the solid form and crystallized.

The properties of the concentrated acid have been lately examined by Dr. Roscoe (*Proc. of Brit. Assoc.*, Sept. 1861). He procured it as a colorless, heavy (sp .gr. 1·782), oily-looking liquid, highly corrosive, and giving off, when heated in air, dense white vapors. It is one of the most powerful oxidizing agents known ; a single drop brought into contact with charcoal, paper, wood, alcohol, ether, and other combustibles, caused explosive combustion resembling that of the chloride of nitrogen. It could not be kept long, even in sealed glass tubes placed in the dark. It underwent spontaneous decomposition, blowing the glass vessel to pieces. When mixed with water, it produced a hissing noise, with the evolution of great heat, forming a crystalline compound. It could not be distilled without decomposition. The acid contains 61 per cent. of oxygen. The solution has a strongly acid reaction, but no bleaching properties.

Perchlorates. Oxychlorates.—These salts have the formula $MO+ClO_7$. Although more abundant in oxygen, they are of less explosive tendency, and less easily decomposed by heat than the chlorates, like which they are resolved either into chlorides and oxygen gas, or into lower oxides, oxygen, and chlorine : they are all soluble in boiling water, but the perchlorate of potassa requires 150 parts of cold water to dissolve it. A perchlorate is known from a chlorate by the non-production of peroxide of chlorine when strong sulphuric acid is added to it.

CHLORINE AND HYDROGEN.—There is only one compound of these elements —an anhydrous gaseous hydracid, known as hydrochloric or muriatic acid gas. It was discovered by Priestley in 1772.

HYDROCHLORIC ACID ($HCl=37$). *Chlorhydric* or *Muriatic Acid.*—Chlorine and hydrogen, when mixed in equal volumes, combine directly to produce hydrochloric acid gas. If a lighted taper is applied to the mixture, or the electric spark is discharged into it, there is immediate combination, with a violent explosion. This also happens when the mixed gases are exposed to the direct rays of the sun, the lime-light, or the light of burning phosphorus. The combination takes place more slowly and gradually in diffused daylight, and is totally arrested in the dark. A mixture of the two gases placed in a graduated vessel over water may be employed for photometrical purposes, the amount of absorption as a result of combination, indicating the intensity of light.

Preparation.—The gas is generally procured by acting upon common salt with sulphuric acid; it must be collected over mercury. The proportions are one part of salt to two parts of acid. The salt should be fused, coarsely powdered, and put into a tubulated retort, which may be one-fourth filled with it: the sulphuric acid should barely cover the salt; the gas is instantly extricated, and when its evolution slackens, it may be quickened by the gentle heat of a lamp. It is convenient to put a long strip of blotting-paper into the neck of the retort, which absorbs any liquid that may chance to go over, and prevents its soiling the mercury. Clean and dry bottles may be filled with this gas by displacement, as it has a high specific gravity. The chemical changes may be thus represented: $NaCl + SO_3,HO = HCl + NaO,SO_3$.

Properties.—Although permanently gaseous at common temperatures and pressures, Mr. Faraday liquefied this gas by generating it in a sealed tube, so as to expose it to a pressure of about forty atmospheres at 50°. It was colorless, and possessed a refractive power inferior to that of water. He could not succeed in solidifying it. (*Phil. Trans.*, 1823; and 1845, p. 163.) Hydrochloric acid gas is perfectly irrespirable; it extinguishes the flame of a taper, and of all combustible bodies, and is itself uninflammable. It irritates the skin; has a strong attraction for water; and when it escapes into the air, it forms visible fumes, arising from its combination with aqueous vapor. A piece of ice introduced into the gas over mercury, is immediately liquefied and the gas is absorbed by the liquid. If a tall jar of the gas be carefully transferred, with its mouth downwards, from the mercurial to the water-trough, the water instantly rushes in with violence, and fills it. The gas has no bleaching properties, but it strongly reddens litmus-paper. In the dry state, it undergoes no change by exposure to heat; but when mixed with air and passed over broken pumice, heated to redness, aqueous vapor and chlorine result. (PELOUZE.)

Water takes up 480 to 500 times its bulk of hydrochloric acid gas, at 40°, and has its specific gravity increased from 1 to 1·210. (H. DAVY.) This may be shown by throwing up a few drops of water into a tall jar of the gas standing over mercury; the gas disappears, and the mercury fills the vessel. There is considerable elevation of temperature during this condensation of the gas. This experiment may be performed like that described at page 194, using a solution of blue in place of red litmus. Entire absorption is a proof of the purity of the gas.

For saturating water with the acid gas, we may employ a tubulated retort or flask, connected with a globe receiver from which issues a tube bent at a right angle, and just dipping below the surface of distilled water contained in a bottle. The bottle should be closed and the water kept cool, as much heat is given out during the condensation of the gas. The different joints of the apparatus may be secured either by grinding, or by well-cut corks rendered tight by a mixture of drying-oil and pipe-clay. The retort or flask may be gently heated by a sand-bath. The bottle should be only half filled with water, as, in dissolving the gas, it increases from one-third to two-thirds in volume.

Solution.—When gaseous hydrochloric acid is thus dissolved in water, it forms the *liquid hydrochloric acid*, commonly called *muriatic acid* or *spirit of salt*, which was discovered by Glauber about the middle of the seventeenth century. It is generally procured by distilling a mixture of dilute sulphuric acid and common salt. The proportions directed in the "London Pharmacopœia" are two pounds of salt and twenty ounces of sulphuric acid, diluted with twelve ounces of water. The retort containing these ingredients may be luted on to a receiver, containing the same quantity of water used in diluting the sulphuric acid, and the distillation carried on in a sand-bath. The specific gravity of the product is stated to be 1·160, and 100 grains of it should be saturated by 132 grains of crystallized carbonate of soda. The following will be found convenient proportions for procuring the acid—6 ounces of salt, previously fused, 8½ ounces by measure of sulphuric acid (sp. gr. 1·65), and 4 ounces of water. An acid of 1·15 sp. gr. is obtained. In order to procure the acid of greater strength (1·21) we may employ the weak acid in place of water and sulphuric acid, in a second distillation with fused salt. (Gregory.) The quantity of real acid in hydrochloric acid of different densities may be ascertained by the quantity of pure carbonate of lime (Carrara marble) which a given weight of the acid will dissolve. Every fifty grains of the carbonate are equivalent to thirty-seven of real acid.

When this acid is pure and concentrated, it should be colorless, but it has generally a pale yellow hue arising from particles of cork or lute that may have accidentally fallen into it, or sometimes from a little iron. The acid of commerce almost always contains iron, sulphuric acid, and sometimes nitric acid, as well as common salt. The iron may be detected by the black tint produced by tincture of galls, in the acid previously diluted and neutralized by carbonate of soda. If a solution of chloride of barium, dropped into the *diluted* acid, occasion a white cloud or precipitate, it announces sulphuric acid. The presence of nitric acid (and of free chlorine and bromine?) is shown by boiling some gold-leaf in the suspected hydrochloric acid, and then dropping into it, a solution of protochloride of tin. If nitric acid be present, this will produce a purplish tint, showing the gold to have been acted upon, which it is not by pure hydrochloric acid. Common salt and other saline substances may be detected in it by evaporating the acid to dryness; when pure, it leaves no residue. Traces of arsenic also frequently exist in hydrochloric acid. This impurity is derived from the sulphuric acid used in its formation. It may be deprived of arsenic by distilling it over a small quantity of sulphide of barium.

The highly concentrated liquid acid (sp. gr. 1·20) is very corrosive, emits copious fumes when exposed to air, and boils, according to Dalton, at a temperature of about 112°; it freezes at —60°. The boiling-point varies with the density of the acid; it is highest (230°) when it contains between 19 and 20 per cent. of the dry gas. (sp. gr. 1·094.) The strong acid becomes weaker, and the weak acid stronger by boiling. It is impossible to expel the whole of the gas by boiling. At a sp. gr. of 1·096, acid and water are distilled over together. When mixed with water, there is a slight elevation of temperature. It is decomposed by many oxacids, such as the chloric, iodic, and bromic acids, and several of the metallic peroxides. Its decomposition by peroxide of manganese, for the production of gaseous chlorine, has already been referred to (page 173). This may be regarded as a good test for the presence of the acid.

When metallic zinc is put into strong liquid hydrocholoric acid, it is rapidly decomposed, and hydrogen is copiously evolved. Some peroxide of lead added to another portion of the acid immediately disengages chlorine, which may be shown by its bleaching power upon a piece of litmus paper; these experiments well illustrate the separation of the two elements of the acid. In the voltaic circuit the chlorine is evolved at the positive electrode or anode, and the hydrogen at the negative electrode or cathode, so that when thus electrolyzed and tinged with indigo, a bleaching effect is produced at the anode. Uncombined hydrochloric acid is not found in nature except as an occasional volcanic product. The acid is an irritant poison to animals, and its vapors are extremely injurious to vegetation; when mixed with 20,000 times its volume of atmospheric air, it proved fatal to plants, shrivelling and killing all the leaves in twenty-four hours.

The following table, by Mr. E. Davy, calculated for 40° and a pressure of 30 inches, shows the strength of hydrochloric acid of different densities:—

Specific Gravity.	100 Grains contain of Hydrochloric Gas.	Specific Gravity.	100 Grains contain of Hydrochloric Gas.
1·21	42·43	1·15	30·30
1·20	40·80	1·14	28·28
1·19	38·38	1·13	26·26
1·18	36·36	1·12	24·24
1·17	34·34	1·05	10·10
1·16	32·32	1·01	2·02

According to Dr. Thompson, the strongest liquid hydrochloric acid (sp. gr. 1·203) contains 1 atom of real acid + 6 atoms of water; when this is evaporated in the air, hydrocholoric acid escapes, and it is ultimately reduced to 1 atom of acid+12 of water (sp. gr. 1·119). This hydrate is said to have a sp. gr. of 1·128 at 58°, and it boils at 223°. When a solution of hydrochloric acid is distilled, a quantity of gas escapes in the first instance; but acid and water soon begin to be distilled together, and the boiling point remains fixed at 230°. This new hydrate has a sp. gr. of 1·094, and it is found to contain 16 atoms of water. There are therefore, according to Bineau, three hydrates of this acid—$HCl,6HO$: $HCl,12HO$: and $HCl, 16HO$. Pure hydrochloric acid of convenient strength for use in the laboratory may be obtained by diluting the strongest acid with about its volume of water, so as to reduce its density to about 1·1, and then distilling it over a little chloride of barium. The acid carries over a sufficiency of water for condensation, which may be effected by Liebig's condenser. Acid of this strength does not fume on exposure to air.

The concentrated acid, at a high temperature, carbonizes and destroys organic matter. It has, generally speaking, no action on non-metallic bodies; and among metals it is not decomposed by gold, platinum, mercury, or silver. If pure, it may be boiled on these metals without change. Its chlorine is taken by lead, tin, zinc, and iron, hydrogen being set free. Its action on copper is peculiar. In the concentrated state and under a free access of oxygen or air, the acid loses its hydrogen, which forms water, and oxychloride of copper is produced. By means of copper and hydrochloric acid, the whole of the oxygen may be removed from a confined volume of a air. (*See* NITROGEN, p. 141.) It is decomposed by the alkaline metals, chlorides being formed, and the hydrogen liberated. Metallic oxides, including the alkalies, decompose it, producing water and a chloride ($KO+HCl=HO+KCl$.) Some bases, however, appear to enter into direct combination with it—among these may be mentioned magnesia, alumina, and, according to some chemists, the oxides of chromium and cobalt. These appear to form both hydrochlorates as well as chlorides. Morphia and the vegetable alkaloids form hydrochlorates only.

Equivalent and Composition.—When equal volumes of chlorine and hydrogen are mixed, and the electric spark is passed through the mixture, the gases unite, without change of volume, to produce hydrochloric acid, which is entirely absorbed by water. If exposed to diffused light over water, they combine and slowly disappear—the water dissolving the compound as it is produced. The synthetic production of this acid gas may be shown by inflaming a jet of hydrogen and introducing it into a jar of chlorine. It will continue to burn and produce hydrochloric acid. By heating potassium in a measured quantity of the gas, the chlorine is removed and the volume of the gas is reduced to one-half—the residue being pure hydrogen. The specific gravity of the gas is 1·2783. This is equivalent to one-half of the sp. gr. of chlorine, plus one-half of the sp. gr. of hydrogen. Hence it is thus constituted:—

	Atoms.	Weights.	Per cent.	Volumes.	Sp. Gr.
Hydrogen	1	1	2·7	1	0·0691
Chlorine	1	36	97·3	1	2·4876
Hydrochloric acid	1	37	100·0	2	2·5567

and 2·5567÷2=1·2783. Compared with hydrogen, its sp. gr. is 18·5; 100 cubic inches weigh 39·59 grains.

Tests.—The gas is known by its acid reaction, great solubility in water, the dense fumes which it produces in a humid atmosphere, and the white fumes of hydrochlorate of ammonia which are evolved when a glass rod, dipped in a strong solution of ammonia, is brought near to it. The production of a solid compound by the combination of the two gases, may be well illustrated by placing a small jar of dry ammonia within a tall stoppered jar. When the ammonia is proved, by its reaction on test-paper, to have reached, by diffusion, the top of the bell-jar, the stopper may be removed and a jar of hydrochloric acid gas placed over the opening. The gases immediately combine, and the hydrochlorate of ammonia formed, descends in a dense white cloud. A *solution* of hydrochloric acid in the concentrated state, may be identified by its evolving chlorine when boiled with peroxide of manganese. In the diluted state, it is recognized by giving a white-clotted precipitate with a solution of nitrate of silver (AgCl) which is insoluble in nitric acid, and becomes slate-colored and ultimately blackens by exposure to light.

NITRO-HYDROCHLORIC ACID. NITRO-MURIATIC ACID.—This term has been applied to the *Aqua Regia* of the alchemists. When nitric and hydrochloric acids are mixed, they become yellow, and acquire the power of dissolving gold and platinum, which neither of the acids possesses separately. This mixture, when heated, evolves chlorine, a partial decomposition of both acids taking place. Three parts of hydrochloric and one of nitric acid, furnish the most effective mixture; but a solution having the same general properties, is obtained by adding nitre to hydrochloric acid, or common salt to nitric acid. In the mutual decomposition of the two acids by heat, chlorine is evolved until one of the acids is entirely decomposed. When a metal is put into nitro-hydrochloric acid, it is not dissolved by either of these acids, but by the nascent chlorine, the metal combining with it as fast as it is evolved. The application of heat greatly accelerates this action, but much chlorine may be lost by employing too high a temperature. The red vapors which escape on heating the mixture may be condensed by distillation. The condensed liquid is known as *Chloronitric* acid, and has the composition NO_2Cl_2. The reaction by which it is produced may be thus represented: ($NO_5HO+3HCl=NO_2Cl_2+Cl+4HO$). Towards the end of the distillation, another compound, called *Chloro-nitrous* acid, is produced. This has the composition NO_2Cl, and is thus formed: ($NO_5,HO+3HCl=NO_2Cl+2Cl+4HO$). This is a gaseous acid of a deep orange-red color; it may be procured by the direct union of deutoxide of nitrogen to one-half of its volume of chlorine. During the solution of metals in this acid, the production of a metallic chloride and of deutoxide of nitrogen, may be thus represented: ($3M+NO_5+3HCl=3MCl+NO_2+3HO$). Nitro-hydrochloric acid is the common solvent of gold and platinum, and may, with proper precautions, be used in the separation of these metals from silver, which remains as an insoluble chloride. It furnishes a useful solution of tin; and is employed in the analysis of minerals containing sulphur, to separate and acidify that substance.

NITROGEN AND CHLORINE. CHLORIDE OF NITROGEN; TER-CHLORIDE OF NITROGEN. NCl_3.—The gases do not unite directly, but the compound may be obtained by exposing a solution of nitrate or hydrochlorate of ammonia to the action of chlorine, at a temperature of 60° or 70°. The gas is absorbed, and a yellow oil-like fluid, heavier than water, is produced by the union of the nascent nitrogen (evolved in the decomposition of the ammonia of the salt) with the chlorine. $NH_3,HCl,+6Cl=4HCl+NCl_3$. It was discovered by Dulong, in 1812, and its properties were afterwards investigated by Davy.

The simplest mode of obtaining this compound consists in filling a perfectly clean glass basin with a solution of 1 part of sal-ammoniac in 12 or 15 of water, and inverting in it a tall jar of chlorine. The saline solution is gradually absorbed and rises into the jar, a film forms upon its surface, and it acquires a yellow color; at length small globules of the pure chloride of nitrogen, looking like a yellow oil, collect upon its surface, and successively fall into the basin beneath. Balard obtained this compound by suspending a piece of sulphate of ammonia in a strong solution of hypochlorous acid.

The specific gravity of chloride of nitrogen is 1·65; it is not congealed by cold. Its odor is irritating and peculiar; it very soon evaporates when exposed to air. It is apparently a non-conductor of electricity. It is dangerously explosive, and is decomposed with violent detonation by mere contact with many combustibles, especially phosphorus, oil of turpentine, and the fixed oils. In making these experiments, great caution is required. Dulong lost an eye and the use of a finger, and Sir H. Davy was wounded in the face, by the effects of its detonation. The explosion takes place with a flash of light, and the vessel containing the substance is shattered. A leaden basin should therefore be used for the experiment. At 160° it distils without change, but at 212° it explodes, and is decomposed.

The production of light and heat in the decomposition of this compound does not admit of explanation on any of the ordinary theories of combustion. In combustion bodies unite, and light and heat are the products of their union and condensation. In reference to this chloride, however, as well as the oxides of chlorine and the iodide of nitrogen, the light and heat are the results of the separation of the elements.

The composition of this chloride, although given as NCl_3, is by some considered to be NCl_4. Its true constitution is not accurately known. From the researches of Millon it probably contains hydrogen. When mixed with concentrated hydrochloric acid it forms ammonia, and chlorine is evolved. It is slowly decomposed by diluted solution of ammonia—hydrochlorate of ammonia is formed, and nitrogen is evolved. Even when kept in water in a stoppered bottle it slowly disappears, while nitric and hydrochloric acids are formed.

CHAPTER XVI.

BROMINE—IODINE—FLUORINE; AND THEIR COMPOUNDS.

BROMINE (BR=78).

History and Preparation.—Bromine was discovered, in 1826, by M. Balard, of Montpelier, in the uncrystallizable residue of sea-water, commonly called *bittern.* A current of chlorine, passed through this liquid, gives to it an orange tint, in consequence of the evolution of bromine from its combinations ($MgBr+Cl=Br+MgCl$). A portion of sulphuric ether is then shaken up with the colored liquid; this abstracts the bromine, acquires a reddish-brown tint, and rises to the surface. The ethereal solution is drawn off and agitated with a strong solution of potassa, by which a solution of bromate of potassa and bromide of potassium is formed: the ether, floating upon the surface, may be separated and used again; the denser liquid is then evaporated to dryness, and the residue, exposed to a dull-red heat, leaves bromide of potassium. Purified bromide of potassium is usually employed for procuring bromine; but the bromide of barium is preferable, as this salt may be obtained entirely free from chloride. The bromide in fine powder is mixed with half its weight of peroxide of manganese, and its weight of sulphuric acid previously diluted with half its weight of water; and the mixture is distilled into a cold receiver containing water, and into which the beak of the retort or condenser just dips. The deep orange-colored vapor of bromine is condensed, and the liquid bromine, which falls to the bottom of the vessel, is separated from the water, and is afterwards dehydrated, if necessary, by distilling it over chloride of calcium [$2(SO_3HO)+KBr+MnO_2 = KO,SO_3+MnO,SO_3+Br+2HO$]. Should the liquid from which bromine is to be obtained contain iodine, this must be first separated in the form of subiodide of copper (Cu_2I), by the addition of a solution of 1 part of sulphate of copper, and 2½ parts of sulphate of iron.

Bromine probably exists in sea-water in the state of bromide of magnesium, but its relative proportion is exceedingly minute. One hundred pounds of sea-water, at Trieste, afforded only 5 grains of bromide of sodium=3·3 grains of bromine: it is there unaccompanied by iodine; and the same is the case, according to Hermbstadt, in the waters of the Dead Sea. In the Mediterranean, on the contrary, iodine accompanies it. Schweitzer found bromide of magnesium in the waters of the British Channel. Sea-water sometimes contains as much as one grain of bromine in a gallon. Bromine is found in the mineral kingdom combined with silver.

The presence of bromine is recognized either in sea-water or in mineral springs, by evaporating the water so as to separate its more crystallizable contents, reducing the remainder to a small bulk, and dropping into a concentrated solution of chlorine. In the absence of iodine, which may be detected by starch, the appearance of a yellow tint announces bromine. It has thus been discovered in many saline springs, in the ashes of marine plants, and in those of some marine animals. Among the saline springs most abundant in bromine are those of Theodorshal, near Kreutznach, in Germany; these are now the chief source of bromine as an article of commerce.

Properties.—At common temperatures and pressures bromine is a deep reddish-brown liquid, of a pungent disagreeable odor, something resembling that of oxide of chlorine, whence its name (βρῶμος, a stench): its specific gravity is about 3 (2·96 to 2·99.) It emits a heavy brownish-red vapor of an offensive and irritating nature at common temperatures. This *vapor* has a specific gravity of 5·3898, and compared with hydrogen, 78; 100 cubic inches of it weigh 166·92 grains. It has the color of nitrous or hyponitric acid. If respired in a diluted state, it causes a sense of suffocation and great irritation in the nose and throat, producing all the effects of a severe cold, sometimes lasting for several days. The vapor is so heavy, that it may be readily poured into and collected in dry jars; it then appears like an orange-colored gas. It bleaches litmus-paper as well as solutions of organic colors (litmus, aniline-red, indigo, and ink) with the same power as chlorine. The dry vapor, like dry chlorine, does not bleach; hence the bleaching probably depends on the decomposition of aqueous vapor and the effect of nascent oxygen. Its affinity for hydrogen is not so great as that of chlorine. If the air has been entirely displaced by the vapor, a lighted taper, inflamed camphor, or ether, introduced into a jar of it, is instantly extinguished. Bromine vapor, therefore, is a non-supporter of ordinary combustion. The vapor produces with ammonia dense white fumes of bromide of ammonium. It decomposes hydriodic acid gas, setting free the purple vapor of iodine when a small quantity of it is poured into a jar containing that gas. It also decomposes the solutions of the alkaline iodides; bromides are formed, and iodine is separated. Place in a large shallow dish a thin solution of starch, to which a solution of iodide of potassium has been added. Allow the vapor of bromine to fall from a bottle containing this liquid, upon the starch ; the blue iodide of starch will be immediately produced. This experiment, at the same time, serves to illustrate the great density of the vapor.

If a jar containing bromine vapor, is inverted over another containing sulphuretted hydrogen, the sulphur is precipitated, and hydrobromic acid is formed. It is almost as effectual as chlorine in destroying foul effluvia, but its vapor is too noxious and irritating to render it practically useful for this purpose.

As a liquid, bromine boils at 145°. It is solidified when cooled to —7·6, and retains this condition up to 10·4. (PELOUZE.) Its vapor, in spite of its density, is so diffusive, that one drop of the liquid placed in a large globe receiver, or jar, will speedily give a color to the whole of the gaseous contents. Bromine is a non-conductor of electricity, and appears in the voltaic circuit at the positive electrode. It suffers no change by transmission through red-hot tubes. It dissolves sparingly in water (1 part in 33), forming an amber-colored solution of an astringent, but not sour taste, from which the bromine escapes by exposure, and rapidly by boiling: when long kept, especially if exposed to light, it becomes acid from the formation of hydrobromic acid. It forms, under certain circumstances, a definite hydrate, which may be obtained by exposing bromine with a small quantity of water to a temperature of 32° ; red octohedral crystals of the hydrate of bromine are then deposited, which continue permanent at the temperature of 50°, and contain 10 equivalents of water. At a higher temperature they are decomposed into liquid bromine and an aqueous solution of it. The hydrate is also obtained by passing the vapor of bromine through a moistened tube cooled nearly to the freezing-point. Bromine dissolves in alcohol, and more abundantly in ether and chloroform :—these two liquids readily separate it from its aqueous solution. It communicates an orange tint to a solution of starch. Antimony burns in it; and it combines with potassium and phosphorus with explosive violence. Its action on alkaline solutions is analogous to that of chlorine and iodine. It stains the skin of a yellow color, and irritates it; it acts as a corrosive upon most vegetable and animal substances, and is fatal to animal life ; a single drop placed in the beak of a bird will kill it.

BROMIC ACID (BrO_5).—This is the only known compound of bromine and oxygen. Bromic acid is obtained by the decomposition of a solution of bromate of baryta by diluted sulphuric acid : sulphate of baryta is precipitated, and a solution of bromic acid is obtained, which may be concentrated by slow evaporation ; at a high temperature it is partly decomposed, and cannot be obtained anhydrous. It is colorless, acid, inodorous, and first reddens, and then destroys the blue of litmus. It is partially decomposed by concentrated sulphuric acid, but not by nitric acid. It is decomposed by sulphurous acid, by sulphuretted hydrogen, and by hydriodic and hydrochloric acids. From the analysis of bromate of potassa, there can be no doubt that the bromic acid is analogous in composition and chemical properties to the chloric and iodic acids. As it is always in the state of hydrate, its proper formula is BrO_5,HO.

Bromates. These salts are represented by $MO+BrO_5$; they are resolved at a red heat, either into bromides and 6 atoms of oxygen, or into 5 atoms of oxygen and 1 of bromine, a metallic oxide being left: they deflagrate with combustibles like the chlorates. They are recognized by evolving bromine, when heated with strong sulphuric acid.

HYDROGEN AND BROMINE. HYDROBROMIC ACID ($HBr=79$).—Bromine vapor and hydrogen do not combine with each other, either under the influence of the sun's rays, or by the application of a lighted taper or the electric spark; but when they are passed through a tube heated to redness, the vapor and gas combine, and hydrobromic acid is produced. This gaseous acid may be procured by gently heating a mixture of 1 part of phosphorus, 12·5 of bromine, and 7·8 of bromide of potassium, with a little water. (MILLON.) Hydrobromic acid is evolved in dense white fumes when bromide of potassium is decomposed by sulphuric acid; $KBr+SO_3,HO=HBr+KO,SO_3$; but in this case a portion of it is decomposed and bromine vapor escapes; $KBr+2SO_3HO=Br+SO_2+KO,SO_2+2HO$. Phosphoric acid is not liable to this objection, hence a strong solution of this acid may be mixed with the bromide of potassium in place of the sulphuric, and the mixture distilled.

This compound, although gaseous at common temperatures and pressures, condenses into a clear, colorless liquid at 100° below 0°: at 124° below 0°, it is a transparent crystalline solid. As a gas it is colorless, of a pungent and highly irritating odor, and yields dense acid vapors when mixed with humid air. It undergoes no change when passed through a red-hot tube, either alone or mixed with oxygen or iodine; but chlorine decomposes it, producing the vapor and drops of liquid bromine, which, being absorbed by mercury, leaves hydrochloric acid. The attraction of oxygen and of bromine for hydrogen, is probably nearly equal; for bromine does not decompose water at common temperatures, nor does oxygen decompose hydrobromic acid; but at a red heat bromine decomposes aqueous vapor, hydrobromic acid is formed, and oxygen is liberated. Hydrobromic acid gas is not altered by mercury, but tin and potassium entirely decompose it; the former requires the aid of heat; but potassium acts at common temperatures, reducing the gas to half its bulk, and forming bromide of potassium. Hence it appears that the constitution of hydrobromic acid is analogous to that of hydrochloric acid, and that it consists of equal volumes of hydrogen and bromine vapor combined without condensation. The weight, therefore, of 100 cubic inches of hydrobromic acid is 84·53 grains, and the gas consists of—

	Atoms.	Weights.	Per cent.	Volumes.	Sp. Gr.
Hydrogen	1	1	1·266	1	0·069
Bromine	1	78	98·734	1	5·389
	1	79	100·000	2	5·458

And $5{\cdot}458 \div 2 = 2{\cdot}729$ sp. gr.; compared with hydrogen, its sp. gr. is 39·5.

Hydrobromic acid gas is rapidly absorbed by water; heat is evolved, and a fuming liquid acid is obtained, which is colorless when pure, but which readily dissolves bromine, and acquires a yellow color. The specific gravity of the densest aqueous hydrobromic acid is 1·486. It boils at 258°·8 and may be distilled at this temperature. The concentrated acid has the formula $HBr,10HO$. The solution is instantly decomposed by chlorine, acquiring a yellow color from the liberation of bromine. Nitric acid also decomposes it, evolving bromine, and forming water and nitric acid. This mixture may be considered a sort of *aqua regia,* as it dissolves gold and platinum. An aqueous solution of the acid may be obtained by passing a current of sulphuretted hydrogen gas into a mixture of bromine and water; but more conveniently by decomposing a strong solution of bromide of barium with sulphuric acid diluted with its weight of water. On distilling the mixture, hydrobromic acid is procured in the receiver.

When heated with any of the peroxides of metals, the acid is decomposed, water is formed, and bromine escapes in vapor. In its reaction on alkalies, a bromide and water result ($KO+HBr=KBr+HO$,) except in the case of ammonia, in which it is supposed that bromide of ammonium is produced: $NH_3+HBr=NH_4Br$.

Bromides.—These salts are readily identified, 1st. By heating them with sulphuric acid and peroxide of manganese, when bromine escapes. 2d. When dissolved in water—by the solution acquiring a yellow color, and the odor of bromine when a solution of chlorine is poured into it. Ether or chloroform may then be used to separate the bromine. 3d. The solution gives a yellowish-white precipitate with nitrate of silver, insoluble in nitric acid, and requiring a large quantity of ammonia to dissolve it. 4th. It gives an insoluble white precipitate with a salt of lead. The insoluble bromides are decomposed by chlorine and strong sulphuric acid, bromine being set free.

Chloride of Bromine.—By passing chlorine through bromine, and condensing the resulting vapors at a low temperature, a reddish-yellow liquid is obtained, having a penetrating odor and disagreeable taste. It is very volatile, emitting a yellow vapor; it is dissolved by water, and the solution destroys vegetable colors.

IODINE. ($I=126$.)

History.—IODINE was discovered in 1811 by M. Courtois, a chemical manufacturer at Paris. It derives its name from the Greek ἰώδης (violet-colored), from the color of its vapor.

It is chiefly prepared at Glasgow from *kelp,* which is the fused ash obtained by burning sea-weeds, and is principally manufactured on the west coast of Ireland, and the Western Islands of Scotland. The long stems of the *Fucus palmatus* are most productive of iodine. Traces of iodine, in the form of iodide of sodium, have been discovered in plants growing near the sea, in sea-water, in sponge, in many saline springs, in certain kinds of coal, and in the coarser varieties of common salt. Vauquelin detected it in some silver ores from Mexico. It has also been found in cod-liver oil, and in the oil of the liver of the skate, as well as in the common oyster. The commercial source of iodine is sea-weed.

Preparation.—For commercial purposes, a lixivium of kelp, containing chiefly iodide of sodium, is employed for the extraction of iodine. It may be readily procured by mixing iodide of potassium with half its weight of peroxide of manganese, and its weight of sulphuric acid, previously diluted with half its weight of water. The materials may be heated in a short-necked retort or flask connected with a large globular receiver which must be kept cool. The changes which ensue may be thus represented: ($2SO_3HO+KI+MnO_2=KO,SO_3+MnOSO_3+2HO+I$.) The iodine is sublimed, and is deposited in a crystalline form in the cool parts of the receiver. The crystals may be washed out of the receiver by a solution of iodine in water, the liquid poured off, and the deposit rapidly dried between folds of blotting-paper. It may be purified by resublimation at a gentle heat. If the alkaline iodide in kelp be associated with a large proportion of chloride, the iodine may be conveniently precipitated as subiodide of copper (Cu_2I), by the addition of a mixed solution of sulphate of copper (one part) and of sulphate of iron (two and a half parts.) The insoluble subiodide of copper, when heated with peroxide of manganese, yields iodine by sublimation.

Properties.—Iodine has a gray or bluish-black color, resembling plumbago; its lustre is metallic, and its fracture when in a mass, is greasy and lamellar. It is a non-conductor of electricity. It is not changed by passing its vapor through a red-hot tube, either alone or over charcoal. It is soft and friable. Its specific gravity, as a solid, is 4·946. It produces a yellow stain upon paper and on the skin, without corroding it. Its smell somewhat resembles that of diluted chlorine; its taste is acrid. It is extremely volatile, and produces a pale violet vapor at a temperature of between 60° and 80°. This vapor may be well brought out by dropping a few grains of iodine into a large globular glass vessel previously heated. At 120° or 130° it rises more rapidly in vapor; at 220° it fuses; and at 350° it boils and produces dense violet-colored fumes, which are condensed in brilliant rhombic plates and octahedra. It may be entirely volatilized by heating it on writing paper. One hundred cubic inches of iodine *vapor* weigh 269·64 grains. Its specific gravity, therefore, compared with air, is 8·7066, and with hydrogen, 126. Like chlorine and oxygen, it is evolved from its combinations at the positive electrode; it is very sparingly soluble in water, this liquid not holding more than one 7000th of its weight in solution. The color of this solution is pale brown; it gives out no oxygen by exposure to sunshine; it, however, slowly loses its color, and gives rise to the formation of iodic and hydriodic acids. Iodine is very soluble in alcohol and ether, forming deep brown solutions. It is soluble in sulphide of carbon, forming a rich crimson-colored liquid. If in a free state, it may be thus detected and removed from strongly colored organic liquids. Chloroform also dissolves and separates it from its aqueous solution, acquiring a rich purple color.

It is said to be destitute of bleaching properties, but this arises from the small amount of iodine dissolved by water. One ounce of a saturated solution contains only about one-sixteenth of a grain. If a few grains of iodide of potassium are dissolved in the water, a much larger amount of iodine is taken up. This aqueous solution has a dark brown color, and slowly acts upon litmus and indigo when added in sufficient quantity so as to give them a light greenish tint. Iodine is very soluble in water containing chloride of ammonium, nitrate of ammonia, or hydriodic acid. Either as a solid, or in solution, iodine is an irritant poison.

The violet color of the vapor of iodine, as well as its peculiar odor, is in many cases a sufficient evidence of its presence; a more delicate test, however, is furnished by its property of forming a deep blue compound with starch. According to Stromeyer, a liquid containing only one 450,000th of its weight of iodine, receives a reddish-blue tinge when a solution of starch is added to it, provided too much starch is not present. To insure success, the iodine should be in a free state, and the solution cold, for heat destroys the color. When the proportion of iodine is very minute, a few minutes may elapse before the discoloration ensues. When a very minute quantity of iodide of sodium or potassium is present in a solution, the addition of chlorine is necessary; and if a solution of starch be then added, the iodine, set free by the chlorine, is detected by the blue color. If too much chlorine or starch is added, the blue color of the iodide is destroyed. One or two drops of strong nitric acid may be employed as a substitute for chlorine. Any compound containing common salt and an alkaline iodide, mixed with a solution of starch, and exposed to voltaic action, yields a blue color at the positive electrode.

The starch-test may be equally applied for the detection of the vapor.

Place a few grains of iodine in a jar of 200 c. i. capacity, previously warmed, and allow the vapor to diffuse by agitation. Now introduce into the jar, in which the vapor is scarcely visible by color, a piece of paper which has been dipped in a solution of starch. The blue color will speedily appear, and become stronger as the paper is lowered into the jar. The slow diffusion of the vapor from the solid may be thus proved. Suspend within a tall bell-jar a slip of bibulous paper soaked in a solution of starch. Invert the bell-jar over a saucer containing a few crystals of iodine. After some minutes, the diffusion of the vapor will be manifested by the blue color acquired by the paper, the change proceeding from below upwards.

The blue compound obtained by adding a solution of iodine to starch is not permanently destroyed by heat. Unless the solution has been so long boiled that the whole of the iodine has been expelled, the blue color will return as the liquid cools. Iodine acts upon iron, zinc, silver, and some other metals, by direct contact. It has no solvent power on gold. When placed on phosphorus, so much heat is evolved that the phosphorus takes fire and burns. In vapor as well as in solution in water, it decomposes sulphuretted hydrogen, and sulphur is precipitated.

Iodine is sometimes adulterated with plumbago, sulphide of antimony, or peroxide of manganese; but these adulterations are easily detected by their insolubility in alcohol, or by the residue left on heating the iodine on mica, so as to volatilize it. The relative quantity of moisture in iodine may be ascertained by heating it in a tube, with twice its weight of fused chloride of calcium, at a temperature not exceeding the boiling-point of the iodine; the iodine may be expelled by a current of air, and the increase of weight sustained by the chloride gives the quantity of water.

Iodine and Oxygen.—Of the compounds of these elements only two have undergone a complete examination, namely, the Iodic and Periodic acids.

Iodic Acid (IO_5).—This compound cannot be obtained by the direct action of oxygen on iodine; it may be procured by boiling iodine for many hours with about five times its weight of the strongest nitric acid. The mixture should be introduced into a flask having a long neck, or into a retort, in order that the iodine, as it sublimes to the upper part, may be returned into the acid, until it disappears entirely: on carefully driving off the nitric acid by heat, the iodic acid remains as a white uncrystalline solid. It may be dissolved in water, and obtained as a crystalline hydrate. By this process four parts of iodine yield four and a half parts of iodic acid.

The aqueous solution of this acid, when concentrated by evaporation, yields a pasty mass, which is hydrated iodic acid, IO_5,HO. This may be crystallized in hexagonal plates, from which some of the water may be driven off by the careful application of a higher temperature. It then becomes $HO,3IO_5$ (360°). At about 700° it fuses, and is decomposed into oxygen and iodine. Iodic acid acts powerfully upon the metals, and with the oxides forms a class of salts called *iodates*. Nitric, sulphuric, phosphoric, and boracic acids do not decompose it; but it is decomposed by hydrochloric, hydrofluoric, hydriodic, oxalic, sulphurous, arsenious, hydrosulphuric, and other acids.

When it is mixed with charcoal, sulphur, and some other combustibles, it forms compounds which deflagrate when heated. The solution of iodic acid is decomposed by several organic substances, as by morphia, narcotine, gallic, and pyrogallic acids; and among salts by the sulphocyanides and hyposulphites, as well as by sulphate of iron. Iodic acid is analogous to the chloric: it is composed of :—

	Atoms.		Weights.		Per cent.
Iodine	1	...	126	...	75·9
Oxygen	5	...	40	...	24·1
Iodic acid	1	...	166	...	100·0

Iodates.—The salts are represented by the general formula MO,IO_5. By heat, they either become iodides, losing six atoms of oxygen, or they lose iodine and five atoms of oxygen, leaving a metallic oxide. Their deflagration with combustibles is less powerful than that of the chlorates; they are not very soluble in water, and their solutions are decomposed by sulphurous acid, iodine being set free. This is the best test for their presence.

PERIODIC ACID (IO_7HO).—When a solution of iodate of soda, mixed with pure soda, is saturated by chlorine, and concentrated by evaporation, a sparingly soluble white salt is obtained, which is a periodate of soda. This is dissolved in the smallest possible quantity of diluted nitric acid, and mixed with nitrate of lead; a precipitate of periodate of lead is thrown down. This is collected and decomposed by a small quantity of diluted sulphuric acid. Periodic acid is not known in the anhydrous state: it may be obtained as a crystalline hydrate by filtering the liquid and evaporating it. The *periodates* are less soluble than the iodates, but like them they are decomposed at a red heat and evolve oxygen.

HYDRIODIC ACID (HI).—Hydrogen and iodine do not readily combine directly; but when they are passed through a red-hot tube hydriodic acid gas is produced by their union. The gas may be produced by the following process suggested by Millon: 10 parts of iodide of potassium are dissolved in 5 parts of water and 20 parts of iodine are added to the solution in a retort. One part of phosphorus in small portions is then added and a gentle heat is applied ($2KI+I_5+P+8HO=HO,2KO,(PO_5)+7HI$). Hydriodic acid passes over, and phosphate of potassa remains in the retort. As it is a very heavy gas, it may be collected by displacement in dry jars. It is decomposed by mercury, and hydrogen is evolved, so that it cannot be collected over that metal.

Hydriodic acid gas is colorless, but fumes strongly in the air, and smells like hydrochloric acid. It reddens vegetable blues. Its specific gravity, compared with air, is as 4.3878 to 1; 100 cubic inches weigh about 135·89 grains. Compared with hydrogen, its specific gravity is as 63·5 to 1. It extinguishes flame, and is not itself inflammable. It is liquefiable under pressure, and becomes a transparent colorless solid at about —60°. It is not permanent at a red heat, for, when passed through a red-hot porcelain tube, it is partially resolved into iodine and hydrogen.

Hydriodic acid gas is not decomposed by dry air, but when water is present the oxygen of the air unites to the hydrogen, and iodine is eliminated and dissolved. The gas is very soluble in water, but in what proportion has not been determined. The saturated solution, exposed to a temperature below 260°, becomes concentrated by loss of water; at about 260° it boils, and may be distilled. The specific gravity of the strongest liquid acid is 1·7. It dissolves iodine. It becomes dark-colored when kept in contact with air, in consequence of a partial separation of iodine, which colors the liquid. The aqueous hydriodic acid is best prepared by passing sulphuretted hydrogen through a mixture of iodine and water: sulphur is deposited, and, on heating and filtering the liquid, a solution of hydriodic acid is obtained, which may be concentrated by evaporation. The solution is decomposed by chlorine, by nitric, sulphuric, arsenic, iodic, and sulphurous acids, and by the protosulphate of iron, the iodine being separated.

When hydriodic acid gas is mixed with oxygen, and passed through a red-hot tube, it is resolved into iodine and water. Its decomposition by chlorine produces hydrochloric acid, sometimes with explosion, and the purple vapor of iodine is rendered evident, but rapidly disappears in consequence of the formation of chloride of iodine. This decomposition is beautifully shown by causing hydriodic acid gas to pass into a jar of atmospheric air, mixed with about a twelfth of its bulk of chlorine; the violet fumes are then more permanent. On the other hand, mercury takes the iodine and sets free hydrogen. A little strong nitric acid dropped into hydriodic acid gas energetically decomposes it, with the evolution of so much heat that the gas is occasionally inflamed.

The composition of hydriodic acid gas is analogous to that of the hydrochloric. It consists of 1 volume of the vapor of iodine and 1 of hydrogen; these produce 2 volumes of the acid. When potassium is heated in the gas it is reduced to half its volume, which consists of pure hydrogen. It is therefore thus constituted:—

	Atoms.	Weights.	Per cent.	Volumes.	Sp. Gr.
Hydrogen	1	1	0·8	1	0·0345
Iodine	1	126	99·2	1	4·3533
Hydriodic acid	1	127	100·0	2	4·3878

Iodides.—These salts may be thus identified: 1. When heated with sulphuric acid and peroxide of manganese, iodine is evolved. 2. When dissolved in water, the iodide (of potassium) is neutral, and has no action on starch. On adding to the mixture a solution of chlorine, or some nitric acid, a deep blue color is produced. 3. The solution gives a pale yellow precipitate with nitrate of silver, insoluble in ammonia: 4, a bright yellow precipitate with a salt of lead (iodide of lead); and 5, a bright scarlet precipitate with a solution of corrosive sublimate (iodide of mercury). The presence of an iodate is detected by adding a solution of tartaric acid. The solution then becomes colored by iodine being set free.

Iodide of Nitrogen (NHI_2).—This compound has been shown to contain hydrogen, as well as nitrogen and iodine. It may be prepared by placing finely powdered iodine for half an hour in a solution of ammonia. The liquid portion is poured from the insoluble dark brown powder, which is the iodide. It should be well washed in water. This compound is dangerously explosive when dry; hence it should be put in small quantities, while moist, on filtering paper, and allowed to dry spontaneously on sheet lead. The slightest contact of a body, or merely dropping the powder through the air or on the surface of water, causes a sudden and violent explosion, with a flash of light and the escape of iodine in vapor. Even under water it will explode by friction. It is slowly decomposed when moist by exposure to air. Boiling water and solutions of potassa and soda decompose it rapidly. It is converted into nitrogen, iodic, and hydriodic acids. It is decomposed by sulphuretted hydrogen, and it loses its detonating properties in the presence of an excess of ammonia. By numerous experiments, M. Bineau has proved that its true formula is NHI_2.

Chlorine forms two volatile and unstable compounds with iodine, ICl (liquid) and ICl_3 (solid).

Chlorine, iodine, and bromine are occasionally so associated as to require separation in analyses. To ascertain the quantity of iodine in the mixed chlorides and iodides of mineral waters, Rose recommends precipitation by nitrate of silver; the mixed chloride and iodide of silver thus thrown down is fused, weighed, and afterwards heated in a tube, and a stream of chlorine passed over it; the iodine is thus expelled, and the whole converted into chloride of silver; this is weighed again, and a loss is found to have taken place in consequence of the equivalent of the expelled iodine being greater than that of the expelling chlorine; this loss, multiplied by 1·4, gives the quantity of iodine, originally present, which has been replaced by chlorine ($126-36=90$, and $126 \div 90=1{\cdot}4$). Schweitzer recommends the adoption of a similar method for estimating the quantity of iodine when mixed with bromine; in this case the mixed iodide and bromide of silver is to be heated in an atmosphere of bromine vapor, by which the iodine is expelled. The presence of an iodide, in mixture with a chloride and bromide, may be detected by considerably diluting the solution with water, and adding to it a solution of chloride of palladium. Iodine gives with this salt a dense purple black precipitate of iodide of palladium (PdI). A diluted chloride or bromide is not thrown down by this reagent. The mixed sulphates of iron and copper (*see* page 189) precipitate the iodine of an iodide in an insoluble form. A chloride is not affected, and a bromide only when the solution is moderately strong.

FLUORINE (F=19).

History and Properties.—Fluorine is a simple body concerning which in its pure state, but little is known. It is most abundantly met with in the mineral known as fluor or *fluor-spar*, which is a fluoride of calcium (CaF). Hence the name *fluorine.* In its pure state the fluoride of calcium contains 49 per cent. of fluorine. This mineral is found abundantly in Derbyshire, Cornwall, and Cumberland. It is well known by its cubic crystals, sometimes colorless, but more commonly colored purple, yellow, or green. The mineral *cryolite*, from which aluminum is extracted, is a compound fluoride of aluminum and sodium ($Al_2F_3,3NaF$). It is a white translucent fusible substance found in Greenland. It contains about 42 per cent. of fluorine. Fluorine is a constituent of the topaz: it is found in some kinds of mica, in fossil bones and coprolites. It exists in traces in sedimentary rocks, in river, spring, and seawater, in recent bones, in teeth, and in many organic substances.

Davy and other chemists have attempted to isolate fluorine by heating dry fluoride of silver in a current of chlorine. In operating in glass or platinum vessels, the fluorine instantly entered into combination with the silicon or platinum, and fluorides of silicon and platinum alone were obtained. It is stated that fluorine has been procured by the substitution of vessels of fluorspar for those of glass and platinum; but the description of the properties of the body thus obtained, shows that it was probably a mixture of chlorine and hydrofluoric acid. One fact, however, has been elicited as a result of these experiments. When an anhydrous fluoride in a state of fusion is submitted to electrolysis, there is evolved at the positive electrode, a body which decomposes glass and forms with platinum a fluoride which is decomposed by heat. Hence it may be assumed that fluorine, whether gaseous, liquid, or solid, is an electro-negative metalloid, bearing some analogy to chlorine, bromine, and iodine. It forms no known compounds with these elements, with oxygen, or carbon. It unites readily to metals forming fluorides, and to three non-metallic bodies—namely, hydrogen, boron, and silicon. The principal compound of fluorine, is that which it forms with hydrogen—hydrofluoric acid.

HYDROFLUORIC ACID (HF).—This was formerly called fluoric acid, from the supposition that it was a compound of fluorine and oxygen. It is a gaseous anhydrous acid analogous to the hydrochloric. The existence of this acid was first made known by Scheele, although as he employed vesssels of glass, he did not obtain it in a pure state. Its properties were examined by Gay-Lussac and Thénard in 1810 (*Recherches Physico-chimiques*), and by Davy (*Phil. Trans.* 1809-1813). When finely powdered *fluoride of calcium* or *fluor-spar*, as it is usually called (carefully selected for its purity and freedom from silica), is distilled with twice its weight of sulphuric acid, a highly volatile and corrosive liquid, which is hydrated *hydrofluoric acid*, is obtained: $CaF+SO_3,HO=CaO,SO_3+HF$. It acts powerfully on glass and on most of the metals: the retort employed in the experiment may be of lead, with a tube and receiver of platinum; the receiver must be immersed in a mixture of ice and salt. The product may be preserved in a platinum bottle, with a well-fitted stopper of the same metal, but gutta-percha bottles are now commonly employed. In this concentrated state it is a clear, colorless liquid; it fumes when exposed to air; boils at 68°, and flies off in vapor. Its specific gravity in this state is 1·0609. It has not been congealed. By the gradual addition of a certain proportion of water it acquires a considerable increase of density, the mixture having a specific gravity of 1·15 ($HF,4HO$). Its attraction for water exceeds that of oil of vitriol; and when dropped into water it causes a hissing noise, and great heat is evolved. Its vapor is dangerously pungent and irritating, and the liquid acid is eminently active upon organic substances; a minute drop of it upon the skin produces a painful sore, and in larger quantities malignant ulceration: hence the vessels containing it require to be handled with great caution. Its most characteristic property is the energy with which it acts upon glass: its vapors soon destroy the polish and transparency of all neighboring glass-vessels, and when dropped upon glass, great heat and effervescence are produced, and dense fumes are evolved, consisting of *hydrofluosilicic acid.* Diluted with about six parts of water, the acid may be used for etching upon glass, which it effectually accomplishes in a few minutes. For this purpose the surface is covered with a thin layer of wax and tallow, and this is removed from those parts on which it is intended the acid should act. The diluted acid is then poured on the glass, and after a short time it is removed. The layer of wax is melted off, and the pattern then appears corroded on the glass. If a prepared plate is exposed to the acid vapors, a dull surface is given to the corroded portions.

When the concentrated acid is submitted to electrolysis, hydrogen is evolved at the negative electrode, and the positive platinum wire is corroded and converted into a brown compound, probably of fluorine and platinum. All the metals excepting mercury, gold, silver, platinum, and lead, decompose it with the evolution of hydrogen; and peculiar compounds result, *fluorides,* consisting of the metal in combination with fluorine. The action of potassium upon the concentrated acid is very energetic; it is attended by explosion, by the liberation of hydrogen, and by the formation of a peculiar soluble saline compound which is considered as a fluoride of potassium.

The only metalloids on which it acts are boron and silicon. Like hydrochloric acid, it acts violently upon zinc and aluminum, setting free hydrogen; but it has very little action on copper. When added to solutions of lime, baryta, strontia, magnesia, and alumina, it throws down insoluble fluorides of the metals. In this respect it differs from the hydracids of chlorine, bromine, and iodine, which form soluble compounds with these bases. Nitrate of silver produces with this acid a white compound, which is soluble in water, which is not affected by light, and easily decomposed by heat. The chloride, bromide, and iodide of silver are entirely different in their properties. Its most remarkable property is that of acting upon silica and all its combinations, even upon glass—a substance which is not attacked or dissolved by any other acid. A small quantity of the acid poured upon glass produces immediately an opaque spot or streak ($SiO_3+3HF=3HO+SiF_3$).

The fluoride of silicon produced when in contact with water undergoes a change by which hydrated silicic acid is precipitated.

This acid, when mixed with strong nitric acid, and the mixture is heated, does not dissolve gold or platinum. It forms no aqua regia, like the hydrochloric acid.

Composition.—Kuhlman's experiments have proved that this is a hydracid; he found that pure fluor-spar (fluoride of calcium) was not in the least acted upon, even at a red heat, by anhydrous sulphuric acid, and that when hydrochloric acid was transmitted over fluor-spar at a red heat, hydrofluoric acid was disengaged and chloride of calcium formed. It cannot therefore be doubted that the hydrofluoric, like the hydrochloric acid, is composed of one atom or volume of each of its elements, and it may be assumed that they are united without any condensation.

	Atoms.		Weights.		Per cent.		Volumes.
Hydrogen	1	=	1	...	5	...	1
Fluorine	1	=	19	...	95	...	1
	1		20		100		2

Its atomic weight is derived from the proportion of sulphate of lime obtained by the decomposition of a known weight of pure fluoride of calcium.

Fluorides.—A soluble fluoride is known by its action on glass. An insoluble fluoride may be powdered and covered with sulphuric acid in a platinum crucible. If the substance is a fluoride, or if any fluoride be present, the vapor set free, will produc a visible change on a glass plate placed over the crucible.

CHAPTER XVII.

SULPHUR AND ITS COMPOUNDS—SELENIUM AND ITS COMPOUNDS.

Sulphur ($S=16$).

This important substance is found native, chiefly in volcanic districts, either crystallized or amorphous. The Island of Sicily, and the Solfatara, near Naples, are the principal sources of supply. There are large deposits of sulphur in Spain, also around Hecla, in Iceland, and it occurs more sparingly in certain gypsum beds in Europe. The well-known mineral, iron-pyrites, contains about 54 per cent. of sulphur, and readily yields this substance by distillation. The sulphur thus obtained is, however, less pure than native volcanic sulphur, and is generally contaminated with arsenic. Although commonly described as a mineral body, sulphur enters into the composition of certain animal and vegetable substances. Associated with nitrogen, it is a constituent of albumen, fibrin, and casein; it enters into the composition of silk, hair, horn, nail, and feathers. It is found in gluten, and certain essential oils—*e. g.* those of mustard and horseradish.

Preparation.—The native mineral, on which the sulphur is deposited, is broken up and submitted to distillation in fireclay pots, connected with receivers. The mineral contains from 30 to 50 per cent. of sulphur. The greater part of this is separated by the first distillation, the sulphur thus obtained containing rarely more than 5 or 6 per cent. of earthy impurities. By a second distillation, the sulphur is obtained pure; and while in a liquid state it is poured into wooden moulds of a slightly conical shape. The sulphur, when cooled, is removed, and it then forms the well-known *roll-sulphur* of commerce. By conveying the vapor during distillation into a large chamber, kept cool, the sulphur is deposited in a pulverulent state, and is then known as *flowers of sulphur*. Owing to the combustion of a portion some sulphurous acid is produced, and thus the powder occasionally has an acid reaction from this cause. Sublimated sulphur may be purified by washing it in hot water. Sulphur is obtained from pyrites, by simply distilling the broken mineral in fireclay, or cast-iron retorts, connected with receivers. The mineral yields readily from 20 to 25 per cent. of sulphur, which frequently has a greenish tint, from the presence of some sulphide of iron. Sulphur in its purest form generally contains a trace of hydrogen.

Properties.—Sulphur, or *brimstone,* is a brittle substance, of a pale yellow color, insipid, and inodorous, but exhaling a peculiar odor when rubbed or heated. Its specific gravity is 1·970 to 2·080. According to Regnault, the specific heat of crystallized native sulphur is 0·1776, and of sulphur recently fused, 0·1844. It becomes negatively electrical by heat and by friction, and is a non-conductor of heat and electricity. Sulphur, as a mineral product, occurs crystallized, its primitive form being an acute octahedron with a rhombic base. In this state its sp. gr. is 2·045, and the crystals are in a high degree doubly refractive. Crystals of native sulphur, which have been formed by the condensation of sulphur vapor, as well as those which are deposited from a solution of sulphur in any menstruum, possess forms which are either identical or connected by being referable to the same crystalline axes. Such, on the contrary, as are produced by the cooling of fused sulphur, belong to a different system of crystallization. One of the conditions determining the form, is temperature: if the crystal be formed below 232° it belongs to the right prismatic system; if at that point, to the oblique prismatic. This is proved by the influence of temperature on a crystal of either system; a crystal of fusion, when first formed, is perfectly clear and transparent, but kept at common temperatures it soon becomes opaque, and presents the appearance of the roll sulphur of commerce; the same change occurs when a native crystal is placed in a solution of salt which boils at 232°. The opacity is in both cases produced by a new arrangement of the particles of sulphur, by which, without any change in the external form, the internal structure of the crystal is altered. Sulphur, therefore, is dimorphous. (*See* p. 36.)

Sulphur has no injurious action on the body: it is insoluble in water, and suffers no change by exposure to air. An invisible vapor is constantly escaping from it at common temperatures. If leaf-silver be suspended in the upper part of a bottle containing sulphur, it will, after a few weeks, become blackened by conversion into sulphide of silver. At about 180° sulphur is volatilized, and its peculiar odor is strong and disagreeable; at about 220° it begins to fuse, and between 230° and 270° it is perfectly liquid, and of a bright amber-yellow color. It may be readily melted by heating it on writing-paper over a candle. On cooling it sets into a group of prismatic crystals. If melted on a glass-slide, and examined by an inch-power of the microscope, the phenomena of prismatic crystallization are beautifully seen. When sulphur is heated to between 300° and 500°, it becomes viscid, and of a dark brown color, but regains its fluidity when cooled to 230°. At a higher temperature (out of contact of air) it again becomes more liquid, and at about 800° it boils, producing an amber-colored vapor, which may be condensed either in a solid or pulverulent state, according to the rapidity of the process and the size of the condensing vessels. The residue is the *sulphur vivum* of old pharmacy. If sulphur is heated to about 450°, and while still viscid, is poured into cold water, it acquires and retains a certain flexibility and elasticity, having at the same time a dark color: it hardens slowly. In this state, it is sometimes used to take impressions of gems and medals, or plaster medallions. For this purpose, the surface of the mould should be oiled before the sulphur is poured on it. When cold, it has a reddish-brown color, and a specific gravity of 2·3. When slowly cooled after fusion, sulphur forms a fibrous crystalline mass; but it sometimes retains its fluidity, and does not concrete till touched by some solid body. This state appears somewhat analogous to that of water cooled in a quiescent state below its freezing-point. (Faraday, *Quarterly Journal*, 21, 392.) (For the method of procuring crystals of sulphur by fusion, *see* page 25.) The following table shows the results of Dumas's experiments on the influence of temperature upon the color and properties of sulphur:—

Temperature.	Hot Sulphur.	Sulphur suddenly cooled by immersion in water.
230°	Very liquid: yellow	Very brittle: usual color.
284	Liquid: deep yellow	Do. do.
338	Thick: orange yellow	Brittle: do.
374	Thicker: orange	At first soft and transparent, then brittle and opaque: usual color.
428	Viscid: reddish	Soft: transparent: amber color.
464 to 500	Very viscid: brown-red	Very soft: transparent: reddish.
800 boiling	Less viscid: brown-red	Do. do. brown-red.

In order that sulphur may retain its soft or viscid state, it is not necessary, as sometimes directed, to keep it long in a fused state, but merely to take care that it has been raised to a due temperature, and then suddenly cooled by dropping it into cold water; if poured into the water in mass, the interior cools slowly and reverts to its brittle state. Here, therefore, the effect of what may be called *tempering*, is the reverse of that produced upon steel, and somewhat corresponds with the phenomena presented by bronze.

The researches of Deville, Berthelot, Magnus, and other chemists, have shown that sulphur, according to the effect of heat and sudden cooling, may assume various allotropic conditions. Deville assigns four varieties, and Magnus six. These are based chiefly on crystalline form, color, and solubility. The *black* sulphur of Magnus is obtained by heating sulphur repeatedly to near its boiling-point, and then suddenly cooling it in water. It is characterized not only by its color, but by its insolubility in sulphide of carbon, and the usual solvents of sulphur. (Pelouze and Fremy, *Traité de Chimie*, 1, 200.) The sulphur of commerce occurs in three prevailing colors, namely, lemon yellow, verging on green, dark yellow, and brown yellow; these shades result, partly at least, as the above table shows, from the different degrees of heat to which it has been exposed during its fusion or extraction on the great scale—the palest variety having been the least heated.

For some pharmaceutical purposes, sulphur is precipitated from a solution of tersulphide of potassium or pentasulphide of calcium, by hydrochloric acid, and, when washed and dried, it forms a pale yellowish-gray impalpable powder; this is the *milk of sulphur* and *precipitated sulphur* of the Pharmacopœia. Thomson considers it to be a compound of sulphur and water—*a hydrate.* (*System of Chemistry*, vol. 1, p. 285.) When dried it gives out no water, but fuses into common sulphur, always, however, evolving a little hydrogen.

The purity of sulphur may be judged of by heating it gradually upon a piece of mica or platinum-foil; if free from earthy substances, it should evaporate and leave no residue. It should also be soluble in benzole or boiling oil of turpentine. According to Ure, sulphur is soluble in ten times its weight of boiling oil of turpentine at 316°, forming a red-colored solution which remains clear at 180°. When the solution cools rapidly, or is rapidly evaporated, prismatic crystals are deposited. If, however, it is allowed to evaporate spontaneously, octahedral crystals are formed. The same phenomenon is observed in reference to the solution of sulphur in benzole. The employment of either of these liquids enables a chemist to determine whether sulphur is contaminated with its usual impurities, namely, carbonate and sulphate of zinc, oxide and sulphide of iron, sulphide of arsenic and silica. These remain undissolved.

The sp. gr. of sulphur-vapor is theoretically 6·6336, and, supposing it to exist as vapor at mean temperature and pressure, 100 cubic inches would weigh 205·44 grains. From the experiments of Dumas and Mitscherlich, at a temperature of 932°, the sp. gr. of the vapor is 6·654. According to Bineau, when taken at a temperature of 1832°, the sp. gr. is 2·218. Compared with hydrogen, the sp. gr. of sulphur-vapor is as 96 to 1.

Sulphur is not readily dissolved by alcohol, ether, or chloroform. Anhydrous alcohol when boiled with it dissolves it in small quantities. The vapors of these liquids also combine with it. It is very soluble in sulphide of carbon; 100 parts of this liquid will dissolve 38 parts of sulphur at the common temperature, and 73 parts when heated. The sulphide may be usefully employed for the separation of sulphur from vulcanized rubber, gunpowder, &c. If recently fused sulphur is dissolved in the sulphide, and it is spontaneously evaporated, crystals belonging to the two systems are deposited, namely, transparent octahedra, and oblique rhombic prisms, which are opaque. It is probable that by heat the sulphur has partially undergone an allotropic change. Among other solvents of sulphur may be mentioned chloride of sulphur and the alkaline sulphites. The latter are commonly used for devulcanizing caoutchouc.

When heated in the atmosphere to about 560° sulphur inflames and burns with a peculiar blue light; at a higher temperature its vapor kindles with a purple flame; and in oxygen it burns vividly, with a large lilac-colored flame. The comparatively low temperature at which sulphur is kindled, is an important circumstance in reference to its use for the manufacture of gunpowder, matches, &c. It may be well illustrated by propelling powdered sulphur into the hot air issuing from an argand lamp-glass; it takes fire at a great height above the flame. The product of combustion is sulphurous acid, known by its peculiar odor.

Equivalent and Compounds.—Sulphur combines with the metalloids and metals, forming the class of *sulphides* or sulphurets. The metallic sulphides generally correspond to the oxides. The range of combination of sulphur is very great; it frequently displaces oxygen, converting oxides to sulphides, while many sulphides, by simple exposure to air, are converted to oxides. Its atomic weight, as deduced from its compound with hydrogen, is 16. Hence as sulphur-vapor has a sp. gr. of 96, compared with hydrogen, each volume of the vapor will correspond to six atoms, or the atomic volume of sulphur-vapor will be one-sixth of a volume. If the atomic volume of hydrogen be two, then that of sulphur will be one-third of a volume.

Tests.—The color, fusibility, and combustion with a blue flame, as well as the odor of the vapor, are sufficient tests for sulphur in a solid state. Its solubility in sulphide of carbon, and the production of octahedral crystals as a result of the spontaneous evaporation of the solution, are also characteristic of the presence of this substance. In many organic solids its existence is revealed by applying heat, when sulphuretted hydrogen escapes. If sulphur, or any substance containing traces of it (quill or gluten), be boiled in a solution of potassa, holding dissolved a small quantity of oxide of lead, the liquid or the solid acquires a brown-black color from the production of sulphide of lead. The test is prepared by adding to a solution of potassa a few drops of a solution of acetate of lead, and then adding a sufficient quantity of potassa to dissolve the white precipitate which is first formed.

SULPHUR AND OXYGEN.—Sulphur forms no oxide; but there are seven compounds of sulphur and oxygen, all of which rank among the acids. The most important of these are, 1. Sulphurous acid; 2. Sulphuric acid; and 3. Hyposulphurous acid.

Sulphurous acid . . .	$S\,O_2$	Hyposulphuric (dithionic) acid	S_2O_5
Sulphuric acid . . .	$S\,O_3$	Trithionic acid . . .	S_3O_5
Hyposulphurous acid } . .	S_2O_2	Tetrathionic acid . . .	S_4O_5
Dithionous acid }		Pentathionic acid . . .	S_5O_5

In the four last compounds, the atoms of oxygen being 5, there is an increase of one atom of sulphur in each. Of the seven oxy-compounds here enumerated, the first three have a special importance to the chemist, and as they are produced by a conversion or reaction of sulphurous acid, it is this compound which will first claim our consideration.

SULPHUROUS ACID (SO_2).—This is an anhydrous gaseous acid produced by the burning of sulphur in oxygen. In 1774, Scheele pointed out a method of obtaining it: and about the same time, Priestley procured it in the gaseous form, and ascertained its leading properties. Its atomic composition was first accurately investigated by Davy, Gay-Lussac, and Berzelius.

Sulphurous acid may be obtained by several processes. It may be procured directly, by burning sulphur in dry oxygen gas; or indirectly, by boiling one part of copper filings or of mercury in three of sulphuric acid ($Cu+2[SO_3,HO]=CuO,SO_3+2HO+SO_2$): or by heating in a retort a mixture of three parts of black oxide of manganese in powder and one of sulphur, $S_2+MnO_2=SO_2+MnS$. Charcoal or sulphur boiled with sulphuric acid, also yields this gas. As water dissolves about fifty times its bulk of the gas, it should be collected and preserved over mercury. For all the common purposes of experiment, it may be collected by displacement in dry jars or bottles. When generated by the action of charcoal, wood, and various organic matters, upon sulphuric acid, it is mixed with carbonic acid. Sulphurous acid may be procured by the combustion of sulphur or sulphide of carbon in a confined volume of air. Under these circumstances, it is mixed with nitrogen or carbonic acid.

Properties.—The gas is without color, but it has the suffocating odor of burning sulphur, and a sour taste. If breathed in a diluted state, it causes cough and headache; and in a concentrated form it is fatal to life. It is highly destructive to all animals. It is very heavy, being more than twice the weight of air. Its sp. gr. is 2·2112, and, compared with hydrogen, 32 to 1; 100 cubic inches weigh 68·48 grains. It is one of the most easily liquefiable of the gases (p. 73). By mere cooling to 14°, it becomes an anhydrous limpid liquid.

In the liquefied state it has a sp. gr. of 1·45, evaporating with such rapidity at common temperatures as to generate a great degree of cold, so that by its aid mercury may be frozen, and chlorine, ammonia, and cyanogen liquefied. The liquid acid is not an electrolyte. When it is allowed to evaporate *in vacuo*, the cold produced is so intense, that the liquid acid is congealed; it solidifies at —105°; it may also be frozen by the aid of a mixture of solid carbonic acid and ether; it then forms a white crystalline mass, denser than the liquid acid.

When sulphur is burned in pure and perfectly dry oxygen, sulphurous acid only is produced, without any change in the volume of oxygen, so that its composition is learned by the increase of weight. Oxygen when saturated, is exactly double in weight; hence sulphurous acid consists of equal weights of sulphur and oxygen. According to Mitscherlich's estimate of the specific gravity of sulphur-vapor, sulphurous acid consists of 100 volumes of oxygen gas, and 16 of the vapor of sulphur, condensed into 100 volumes; or one volume of oxygen combined with one-sixth of a volume of sulphur-vapor constitute one volume of sulphurous acid.

	Atoms.	Weights.	Per cent.	Volume.	Sp. Gr.
Sulphur	1	16	50	$\frac{1}{6}$	1·1055
Oxygen	2	16	50	1	1·1057
Sulphurous acid	1	32	100	1	2·2112

As oxygen undergoes no change of volume in forming this gas, the number of volumes of sulphurous acid are indicated by the quantity of oxygen consumed in the combustion of sulphur.

The *gas* has a strongly acid reaction. It extinguishes most combustibles when they are immersed in it in an inflamed state: hence burning soot in a chimney may be extinguished by throwing a handful of sulphur into the fire. The upper part of the flue should be stopped, and no air allowed to pass into the chimney except that which traverses the burning sulphur. Air containing only one-third of its volume of this gas does not support ordinary combustion. The gas vividly maintains the combustion of potassium and sodium. At mean temperature and pressure, recently boiled water takes up about 50 volumes of sulphurous acid gas. This solution (*aqueous sulphurous acid*), which may be procured by passing the gas into distilled water, has a sulphurous and somewhat astringent taste, and it bleaches some vegetable colors. If long kept, sulphuric acid is formed; it acquires a sour flavor, and reddens vegetable blues. Some coloring matters, such as those of litmus and cochineal, are not readily bleached by sulphurous acid; while those which are bleached may have their colors restored by an acid or an alkali. If a solution of sulphurous acid is added to infusion of roses or blue infusion of cabbage, it will redden these liquids, owing to the presence of free sulphuric acid. By carefully neutralizing this acid with potassa, the color will entirely disappear. If the liquid thus bleached, be now treated with a strong solution of potassa, it will acquire a green color, while another portion will be intensely reddened by sulphuric acid. The bleaching, therefere, depends upon a temporary production of colorless sulphites. Cotton goods, as well as those of silk, woollen, and straw, which would be injured by chlorine, are bleached by this acid. The articles, wetted, are exposed in a close chamber to the fumes of burning sulphur. They are then well washed, to remove the colorless sulphites, and are thus effectually bleached. Hops are also bleached by exposure to the vapor of burning sulphur. Sulphurous acid by its removal of free oxygen arrests fermentation and putrefaction. When the aqueous solution of sulphurous acid is boiled, a great part of the gas escapes, but not when it is frozen. The specific gravity of the solution at 60°, when it contains 50 volumes of the gas, is 1·04. At a low temperature the concentrated aqueous solution deposits a crystalline hydrate consisting of SO_2+9HO. Alcohol dissolves sulphurous acid more copiously than water; one volume taking up at 60°, 115 volumes of the gas.

Sulphurous acid gas suffers no change at a red heat; but if mixed with hydrogen, and passed through a red-hot tube, water is formed and sulphur deposited ($2H+SO_2=S+2HO$). Under the same circumstances, it is decomposed by charcoal, by potassium, and sodium, and probably by several other metals. It undergoes no change when mixed with oxygen, unless humidity or water be present, in which case a portion of sulphuric acid is slowly formed. But a mixture of the dried gases passed over heated spongy platinum, produces anhydrous sulphuric acid. When mixed with chlorine, and in contact with water, sulphurous acid produces sulphuric and hydrochloric acids ($SO_2+HO+Cl=SO_3+HCl$); but the perfectly dry gases have no mutual action, except under the influence of bright summer sunshine, when a mixture of equal volumes of chlorine and sulphurous acid, yields a liquid of the specific gravity of 1·659 at 68°, which boils at 170°, the specific gravity of the vapor being 4·67. Its formula is SO_2,Cl. It may be compared to sulphuric acid, in which one atom of oxygen has been replaced by one of chlorine. With water, it evolves heat and yields hydrochloric and sulphuric acids. Iodine and bromine are without action on sulphurous acid unless water is present, when sulphuric acid, and hydriodic and hydrobromic acids are formed ($SO_2+HO+I=HI+SO_3$). The chloric, bromic, and iodic acids are decomposed by sulphurous acid, with the evolution of chlorine, bromine, and iodine, and the formation of sulphuric acid. When gaseous sulphurous acid is mixed with hydrochloric, hydriodic, or hydrobromic acid gases, they mutually decompose each other; water, with chloride, iodide or bromide of sulphur is formed; but when these acids are in aqueous solution, they do not decompose each other. In the dry state, sulphurous acid has no action on hydrosulphuric acid: but when water is present, or the aqueous solutions of the two gases are mixed, water is produced and sulphur is thrown down ($SO_2+2HS=2HO+3S$). Sulphur and pentathionic acid are sometimes products of this mixture. It is probably by a reaction of this kind, that sulphur is naturally deposited at the Solfatara, and in other volcanic districts. Sulphurous acid deoxidizes the oxacid compounds of nitrogen. Thus in contact with nitric acid, sulphuric acid and deutoxide of nitrogen are produced ($3SO_2+NO_5,HO=3SO_3+NO_2+HO$). Two atoms of sulphurous acid produce hyponitrous acid, and one atom produces nitrous acid, both of which are dissolved in the undecomposed nitric acid, giving to it a bluish green or green color. An excess of sulphurous acid therefore entirely decomposes the acid compounds of nitrogen and oxygen. On evaporation of the mixture, nothing but sulphuric acid is obtained: the deutoxide of nitrogen escaping as a gas. Iodic acid undergoes a similar deoxidation, ($5SO_2+IO_5=I+5SO_3$). Iodine is set free, and may be detected by its odor, or by its action on a solution of starch. Sulphurous acid gas is entirely absorbed and removed by peroxide of lead, $PbO_2+SO_2=PbO,SO_3$. In the presence of water or of certain bases, sulphurous acid and deutoxide of nitrogen combine to form crystalline compounds. Peroxide of lead, or of manganese, added to the aqueous solution of sulphurous acid, converts it into sulphuric acid, and destroys its odor.

Tests.—The best test for sulphurous acid gas is its odor, and acid reaction. Paper wetted with a solution of protonitrate of mercury is blackened by it. A mixture of iodic acid and starch in solution, or paper immersed in this liquid, reveals the presence of the smallest quantity of the acid by the production of blue iodide of starch. Zinc is dissolved by the aqueous acid without any evolution of hydrogen ($2Zn+3SO_2=ZnO,S_2O_2+ZnO,SO_2$). If hydrochloric acid is added to the mixture, sulphuretted hydrogen is produced and evolved. Traces of sulphurous acid may thus be found in hydrochloric acid. Sulphurous acid may be detected in the smoke of coke and coal, and it is thus imparted to the atmosphere of places where coal is burnt.

Sulphites and Bisulphites (MO,SO_2 and $MO,2SO_2$).—The *sulphites* of the alkalies when exposed in a moist state to the air, pass gradually, by absorption of oxygen, into sulphates. Chlorine, nitric acid, and several other oxidizing agents, produce a similar change. Sulphites destroy the color of a solution of permanganate of potassa, and reduce the persalts of iron to the state of protosalts; added to nitrate of silver they form a white precipitate of sulphite of silver; which is soluble in nitric acid at a boiling temperature. The precipitate given by nitrate of baryta in the solution of a sulphite (free from sulphate), is also soluble in nitric acid. When an alkaline sulphite is boiled with nitric acid, fumes of sulphurous acid and nitrous acid are evolved, and nitrate of baryta will now produce in the liquid a white precipitate of sulphate of baryta, which is insoluble in nitric acid. A sulphite reduces the chloride of gold from its acid solution slowly in the cold, but rapidly by heat. Arsenic acid is converted into arsenious acid by boiling it with a sulphite or with sulphurous acid. Bisulphite of soda is occasionally used in analysis for the removal of chlorine from liquids. The solid sulphites evolve sulphurous acid, when concentrated sulphuric acid is poured on them. This may be detected by iodic acid and starch.

SULPHURIC ACID (SO_3). OIL OF VITRIOL (HO,SO_3).

Production.—This acid was first obtained by the distillation of sulphate of iron, or *green vitriol,* and was termed, from its appearance and consistency, *oil of vitriol.* It was formerly procured by the combustion of a mixture of eight parts of sulphur and one part of nitrate of potassa or soda in a furnace. During this combustion sulphurous acid and nitric as well as nitrous acid were evolved. It is now found more convenient to produce the sulphurous acid by burning sulphur or iron-pyrites under a regulated current of air in a furnace, and to decompose the nitrate of potassa or soda by means of sulphuric acid, in vessels or pots exposed to the heat of the burning sulphur—or in a separate chamber. The vapors are carried by the flues into capacious leaden chambers, which are sometimes 100 feet long, 20 to 30 feet wide, and 10 to 16 feet high. On the floor of these chambers there is a stratum of water; and the decomposition of the gases by which sulphuric acid is produced, is effected by the occasional introduction of jets of steam. The water on the floor of the chamber dissolves the products, and gradually becomes more and more acid: it is converted into diluted sulphuric acid. When it has thus acquired a specific gravity of 1·2 to 1·3, it is drawn off into shallow leaden boilers, where it is evaporated until it reaches a specific gravity of 1·70. In addition to the loss of water by evaporation, any traces of sulphurous or nitric acid, are then expelled. At this density the acid would begin to act upon lead, and the heat required for its further evaporation, would endanger the softening of the metal. At this degree of concentration, therefore, the acid is run off into boilers, or into stills of platinum, which are set upon cast iron, and in which the further boiling down of the acid is continued until vapors of sulphuric acid begin to appear, or it has attained the specific gravity of 1·84. It is then drawn off by a syphon into a platinum cistern or cooler, and is thence transferred into *carboys,* or large bottles protected by basket work, each holding about 100 pounds of the acid. Before the introduction of platinum vessels, the evaporation was finished in glass retorts.

In this process the sulphurous acid derived from the combustion of sulphur or pyrites is oxidized and converted into sulphuric acid by the agency of deutoxide of nitrogen and water. The nitric and nitrous acids, set free from the nitre, are deprived of three and two equivalents of oxygen respectively and sulphuric acid and deutoxide of nitrogen result ($5SO_2+NO_5+NO_4=5SO_3+2NO_2$). As there is air in the chamber, the deutoxide of nitrogen is immediately converted to nitrous acid ($2NO_2+O_4=2NO_4$) and the nitrous acid thus produced, is again decomposed by the sulphurous acid. It will be perceived from this statement, that the deutoxide of nitrogen, once formed, serves as a medium for transferring the oxygen of air in the chamber to the sulphurous acid ; and the operation is made continuous by allowing a certain quantity of air to pass into the chamber with the sulphurous acid. The amount of sulphuric acid produced, depends on the supply of sulphurous acid. Only a comparatively small proportion of deutoxide is needed for the change.

Dry sulphurous and nitrous acids have no action on each other. The presence of a small quantity of aqueous vapor brings about their combination, and a white crystalline solid is produced. This is decomposed by the water or steam, and while deutoxide of nitrogen is evolved, sulphuric acid is dissolved in the liquid. The composition of these crystals is viewed differently by different chemists, but the following equation indicates the changes : $2SO_2+NO_4,+2HO=2(SO_3,HO)+NO_2$.

The phenomena connected with the production of sulphuric acid may be easily witnessed by introducing sulphurous acid with nitrous acid vapor into a large glass globe, and adding water in a small quantity to produce the crystals, and afterwards in larger quantity to decompose them. In the working chamber, the crystals are not commonly produced, as the jets of steam introduced and the abundance of water prevent their formation. Other methods of forming sulphuric acid have been proposed, but they have not been hitherto applied on a large scale.

Properties.—Monohydrated sulphuric acid is a heavy oily-looking liquid —limpid, colorless, and inodorous. It gives off no vapor at common temperatures. The specific gravity of the pure acid is 1·842 at 60° (PELOUZE). Dr. Ure states that he has met with it as high as 1·845, and Dr. Lyon Playfair has procured it as high as 1·8479. Sulphuric acid boils at a temperature of about 650°, which, therefore, approaches a red-heat, and it may be distilled over without decomposition. Its boiling-point diminishes with its dilution; when of the specific gravity of 1·78 it boils at 435° ; and at 348° when its specific gravity is 1·63. Owing to the small amount of heat rendered latent by the vapor of sulphuric acid, it boils with explosive violence, and gives off sudden jets of vapor. This may be obviated by introducing into the liquid, broken glass or portions of platinum foil or wire. The vapor is readily condensed by mere cooling : it is not necessary to place the receiver in cold water. The concentrated acid freezes at —30° ; and at the same time contracts considerably in its volume. When once frozen, it retains its solid state until the temperature rises to about the freezing-point of water. Sulphuric acid of a specific gravity of 1·78 (which is a definite hydrate, containing one atom of anhydrous sulphuric acid, and 2 atoms of water,) freezes at 40°, but if the density of the liquid be either increased or diminished, a greater cold is required for its congelation.

Sulphuric acid is intensely acrid and corrosive ; it acts speedily upon the skin, occasioning a biting sensation, and a soapy feel of the part, in consequence of its chemical action on the cuticle ; its taste, even when very largely diluted, is extremely acid, and it powerfully reddens litmus. It has a strong attraction for water, so that it absorbs aqueous vapor from the atmosphere and increases rapidly in bulk ; in moist weather three parts increase to four in the course of 24 hours, and by longer exposure a larger quantity of water is taken up, so that it requires to be preserved in well-closed vessels. It is this property which renders it applicable to the drying of certain gases, and to the purposes of evaporation and desiccation under the exhausted receiver of the air-pump. When sulphuric acid is suddenly mixed with water, mutual condensation ensues, and much heat is evolved. Four parts by weight of acid, specific gravity 1·84, and one of water at 60° produce, when thus mixed, a temperature =300°. According to Dr. Ure, the greatest heat is evolved by mixing 73 of acid with 27 of water. Even a boiling temperature does not prevent sulphuric acid taking up moisture from the air; hence it cannot be concentrated so well in an open as in a close vessel; on which account retorts, or large platinum stills, are used for the last stage of its concentration, by manufacturers. The mixture of sulphuric acid with ice or snow causes its immediate liquefaction, and as this liquefaction, consistently with the theory of latent heat, produces cold, while on the other hand the union of the acid with the water evolves heat, the resulting temperature of such a mixture depends upon the relative proportions of the substances mixed. Four parts of acid and one of snow, or pounded ice, evolve heat; but four parts of snow and one of acid, generate cold. Its affinity for water is so great that it will dehydrate and render colorless, crystals of sulphate of iron and sulphate of copper. At the boiling-point it will decolorize Prussian blue; but the blue color is restored on adding water.

Sulphuric acid, under ordinary circumstances, displaces the greater number of other acids from their combinations; thus, in the humid way, it decomposes the phosphates and the borates; at a red heat, however, the phosphoric and the boracic acids, which are comparatively fixed in the fire, expel sulphuric acid from its salts. A solution of sulphate of lime is decomposed by oxalic acid, which forms an insoluble oxalate of lime; and the tartaric, racemic, perchloric, and picric acids decompose sulphate of potassa in solution. In consequence of its strong affinity for water, sulphuric acid chars most organic substances; it acquires a brown tinge from the smallest particles of straw, cement, or dust, that accidentally fall into it; it appears capable of dissolving small portions of charcoal, and also of sulphur, tellurium, and selenium; these substances give to it various tints of brown, red, and green, or blue, and are precipitated when the acid is diluted with water; but if heat be applied, they are oxidized at the expense of the acid, and sulphurous acid is evolved.

When heated with charcoal, sulphuric acid gives rise to the production of carbonic and sulphurous acids ($C+2SO_3=CO_2+2SO_2$): with sulphur, sulphurous acid is the only product ($S+2SO_3=3SO_2$). It is decomposed by several of the metals, which become oxidized and evolve sulphurous acid, as shown in the production of this acid by boiling sulphuric acid with copper, silver, mercury, tin, or lead. Gold and platinum are not affected by the acid even at the boiling-point. When metals, such as zinc and iron, are acted on in the cold by diluted sulphuric acid, the water only is decomposed, its oxygen, being transferred to the metal, forms a metallic oxide, which unites to the undecomposed sulphuric acid to form a sulphate of the oxide, whilst the hydrogen is evolved in the gaseous form.

The strength of sulphuric acid is generally determined by its specific gravity, after its freedom from any solid impurities has been determined by evaporation. According to Dr. Ure, the proportion of dry acid contained in 100 parts of liquid acid at different specific gravities is as follows:—

Specific gravity.	Dry acid in 100.	Specific gravity.	Dry acid in 100.	Specific gravity.	Dry acid in 100.	Specific gravity.	Dry acid in 100.
1·8460	81·54	1·6630	61·97	1·4073	42·40	1·2032	22·83
1·8233	75·02	1·5760	55·45	1·3345	35·88	1·1410	16·31
1·7570	68·49	1·4860	48·92	1·2645	29·35	1·0809	9·78

In ascertaining the specific gravity of sulphuric acid, the temperature requires minute attention, because from the small specific heat of the acid it is easily affected, and because it greatly influences the density. When accuracy is required, the strength of the acid may be determined by its saturating power. For this purpose, a given weight of the acid is diluted with six or eight parts of water, and a solution (of known strength) of pure carbonate of soda added until the solution is exactly neutral (see *Alkalimetry*). Every

54 parts of anhydrous carbonate of soda are equivalent to 40 parts of the anhydrous acid, or to 49 of the liquid sulphuric acid, or oil of vitriol, of the specific gravity of 1·84. Besides lead and potassa, tin and arsenic are sometimes found in sulphuric acid: the tin and lead are derived from the leaden chambers, and the arsenic from the sulphur or pyrites. The methods of detecting these impurities will be described under the respective metals.

Tests.—*The concentrated acid.*—1. It carbonizes a splint of wood introduced into it. 2. It evolves sulphurous acid when boiled with metallic copper. 3. Diluted with its volume of water, heat is evolved. *The diluted acid.*—In the most diluted state a salt of baryta, added to the liquid, throws down a white precipitate of sulphate of baryta, which is insoluble in acids and alkalies. Diluted sulphuric acid does not carbonize organic matter until the water has been driven off by heat, and the acid is thus concentrated. A streak of the diluted acid on paper, when heated, produces a black mark by carbonizing the paper. Pure sulphuric acid should leave no residue on evaporation.

The presence of nitric or nitrous acid is indicated in sulphuric acid by the change of color produced on adding a few drops of a concentrated solution (or a crystal) of protosulphate of iron; a solution of narcotine is also reddened by sulphuric acid containing nitrous acid. Sulphurous acid is detected by its odor and by discharging the color of permanganate of potassa.

ANHYDROUS SULPHURIC ACID (*Sulphuric Anhydride*).—When crystallized green vitriol, or protosulphate of iron, is exposed to a dull red heat, it crumbles into a white powder, and loses the greater part of its water of crystallization. In this state, if put into a coated earthen or green glass retort, and gradually exposed to a full red heat, a dark-colored liquid is distilled over, of a specific gravity of about 1·89. This has been called *Nordhausen*, or *Saxon sulphuric acid:* it evolves a vapor when exposed to air, owing to the escape of the highly volatile *dry* sulphuric acid, which is united in the brown liquid to a portion of hydrated acid. The brown, fuming acid is a ready and perfect solvent of indigo. It is resolved by heat into the common and the anhydrous acid. The changes which take place in its production may be thus represented: $2(FeO,SO_3)=SO_3+SO_2+Fe_2O_3$; but the sulphate of iron is not entirely dehydrated, so that a portion of hydrated acid is distilled over at the same time. The Saxon acid is generally supposed to be thus constituted: SO_3+SO_3,HO; but the proportion of hydrated acid is subject to variation.

The dry or *anhydrous* sulphuric acid may be separated from this brown (or Nordhausen) acid, by a careful distillation from a retort into a dry and cold receiver; it passes over in drops, which concrete, on cooling, into a tenacious crystalline mass resembling asbestos. The acid is liquid at temperatures above 66°; and at 78° its specific gravity is 1·97. When it has once congealed, it is difficult to fuse it, because the first portions heated become vapor, and propel the rest forward; by slight pressure, however, this may be prevented. When kept at a temperature between 75° and 80°, it gradually liquefies. At a temperature of 110°, it boils and evolves a colorless vapor, the density of which, according to Mitscherlich, is 3. The calculated density is 2·77, so that 100 cubic inches would weigh 85·969 grains. In the absence of all moisture, it has no action upon litmus-paper. Passed through a red hot porcelain tube, anhydrous sulphuric acid is resolved into one volume of oxygen and two of sulphurous acid. Caustic lime or baryta, heated in its vapor, becomes ignited, and is converted into sulphate. The attraction of this anhydrous acid for water, is such as to produce intense heat and a hissing noise when small portions of it are thrown into that liquid; and if a sufficient quantity of it be added to such a proportion of water as is required to convert it into hydrated acid, they combine with heat, light, and explosion.

Anhydrous sulphuric acid may also be obtained by the action of anhydrous phosphoric acid upon monohydrated sulphuric acid. (Barreswill.) The phosphoric acid is put into a stoppered retort surrounded by ice and salt, and the oil of vitriol gradually added so as to prevent a rise of temperature, to the amount of two-thirds of the weight of the phosphoric acid; the retort is then removed from the freezing mixture, and a receiver placed there, to which the retort is adapted; on applying a gentle heat, the anhydrous sulphuric acid is distilled over, and is condensed in white silky crystals in the cooled receiver. The principal requisite precaution in this process, is to keep the acids sufficiently cool, whilst mixing them in the retort (*Pharm. Journ.*, 8, 127.) It has also been procured by distilling at a high temperature the dry bisulphate of soda.

It appears, then, that this extraordinary substance, which is thus volatile and easy of congelation, forms, by combining with water, the fixed and with difficulty congealable *oil of vitriol*, and that it contains sulphur and oxygen in the same proportions as they exist in the acid of the dry sulphates. From its resolution when passed through a red hot tube, into one volume of sulphurous acid and half a volume of oxygen, and likewise from the experiments of Berzelius upon the direct acidification of sulphur, it appears that the *anhydrous* sulphuric acid consists of:—

	Atoms.	Weights.	Per cent.
Sulphur	1	16	40
Oxygen	3	24	60
Anhydrous sulphuric acid	1	40	100

The sp. gr. of the vapor is found to be 3·01. Assuming that one volume of sulphurous acid and half a volume of oxygen are condensed into one volume of the vapor, the sp. gr. would be 2·764.

The *liquid hydrated sulphuric acid*, or *oil of vitriol*, when of the sp. gr. 1·846, consists of:—

	Atoms.	Weights.	Per cent.
Dry sulphuric acid	1	40	81·64
Water	1	9	18·36
Monohydrated sulphuric acid	1	49	100·00

The compound of sulphuric acid and water of the specific gravity 1·78, which has been above stated to congeal at 40°, remains solid until the temperature rises to 45°: it is a definite combination of 1 atom of anhydrous acid +2 atoms of water. The acid of specific gravity 1·632, appears also to be a hydrate containing 1 atom of anhydrous acid and 3 atoms of water, for it is to this strength that a diluted sulphuric acid, evaporated *in vacuo* at 212°, is reduced; and it is also in these proportions, that sulphuric acid and water suffer the greatest diminution of bulk in combining. It would appear, therefore, that there are three definite hydrates of sulphuric acid, of which the following are the formulæ, specific gravities, and boiling-points:—

	Formulæ.	Sp. Gr.	Boils at	Congeals at
Monohydrate	SO_3, HO	1·846	650°	—30°
Bihydrate	SO_3,2HO	1·780	435°	40°
Terhydrate	SO_3,3HO	1·632	348°	

Each of these hydrates contains in 100 parts, the following proportions of dry acid and water:—

	Monohyd.	Bihyd.	Terhyd.
Anhydrous acid	81·64	70·94	61·16
Water	18·36	29·06	38·84

According to Dr. L. Playfair, the variation in the sp. gr. of the monohydrated acid, as given by Bineau and Marignac—namely, 1·842 to 1·845—may depend upon the temperature at which it has been distilled. Dr. Playfair found that from an acid of a sp. gr. of 1·848 (81·62 per cent. of anhydrous acid), he obtained a distillate of a sp. gr. of 1·840 (80·12 per cent.). This acid, therefore, lost by distillation one and a half per cent. of anhydrous acid. The weak acid thus obtained, was heated for half an hour to 550°; and after cooling, it gave an acid of 1·8479 (81·61 per cent. of anhydrous acid). Hence it follows, that there is a monohydrate which loses anhydrous acid above 550°, and water below this temperature; so that a strong acid is weakened by being heated above 550°, and a weak acid is strengthened by heating it to a temperature not exceeding 550°. The different temperatures at which the acid has been concentrated, may thus explain the variations recorded in its specific gravity and strength. (*Chem. News*, vol. 3, p. 21.)

Sulphates.—These salts in the anhydrous state are represented by the formula MO,SO_3. Among the alkalies, there are some which form acid sulphates, such as potassa and soda, in which two equivalents of acid are united to one of oxide. These are called *bisulphates* ($MO,2SO_3$). These salts resist a high temperature, but are readily decomposed when heated with two or three parts of charcoal, sulphides of the metals being produced. They are converted into sulphides at a still lower temperature, when heated in a close vessel with cyanide of potassium. An insoluble sulphate, such as that of baryta, is thus easily recognized by its conversion into sulphide. A slight trace of any soluble sulphate, may be detected by the addition of a salt of baryta to the liquid. If a sulphate is present, a white precipitate of sulphate of baryta, insoluble in nitric acid, will be produced.

HYPOSULPHUROUS ACID (*Dithionous Acid*). (S_2O_2).—This acid is only known in the combined state. Its salts, now called Hyposulphites, were originally described by Gay-Lussac (*Ann. de Chim.* 85), under the name of *sulphuretted sulphites.* Thomson first suggested the term *hyposulphurous* for the peculiar acid of sulphur contained in these compounds (*Syst. of Chem.*, 1817), and they were afterwards examined by Herschel. (*Edin. Phil. Journ.*) When an attempt is made to separate the acid from its salts by adding an acid to the solution, sulphurous acid escapes, and sulphur is precipitated. ($S_2O_2=S+SO_2$.)

Hyposulphites.—These salts are formed, 1. When sulphur is digested, at a high temperature but without ebullition, in a solution of a sulphite: in which case the oxygen of the sulphurous acid divides itself between the original and the newly added sulphur: thus we obtain hyposulphite of soda by digesting finely powdered sulphur in a hot solution of sulphite of soda, $NaO,SO_2,+S$, becoming NaO,S_2O_2. 2. When sulphurous acid gas is passed through a solution of an alkaline sulphide, until it no longer precipitates sulphur; thus, we obtain hyposulphite of soda by passing sulphurous acid gas through a solution of sulphide of sodium; in which case $2NaS$, and $3SO_2$, become $2NaO,2S_2O_2,+S$. The properties of the acid may be studied in its salts, and for this purpose the hyposulphite of soda may be selected. This compound is now manufactured on a large scale for the purposes of photography. Hyposulphite of soda dissolves every compound of silver excepting the sulphide, and that portion of a silver salt which has been decomposed by light. Even the insoluble chloride is easily taken up by it, and the solution has a sweetish taste. The acid forms soluble double salts with silver and gold. A hyposulphite precipitates a solution of lead, but redissolves the precipitate when added in excess. Hyposulphurous acid forms soluble compounds with all the alkalies and alkaline earths, excepting baryta, the salts of which are precipitated by a hyposulphite. The admixture of a sulphate is thus easily known: a salt of strontia, which does not precipitate a pure hyposulphite, throws down any sulphate which may exist in it as impurity. A hyposulphite dissolves iodine, destroys the blue color of iodide of starch, and decomposes iodic acid, setting iodine free; but it has no action on iodide of potassium.

Tests.—A hyposulphite may be recognized, 1. By the separation of sulphur and sulphurous acid, when its solution is treated with an acid: 2. By its giving at first a white precipitate with a solution of nitrate of silver, soluble in an excess of the hyposulphite. It dissolves readily the chloride of silver; the bromide, iodide and cyanide are also dissolved by it. If nitrate of silver is added in excess to a solution of a hyposulphite, the white precipitate which is at first formed rapidly undergoes various changes of color, to yellow, brown, and black—sulphide of silver being ultimately formed; 3. By its yielding a black precipitate with protonitrate of mercury; 4. It gives a white precipitate with a salt of lead (hyposulphite) which is soluble in an excess of the solution.

It has been shown by Rose (*Poggendorff's Annalen*, 21), that although the ratio of the sulphur to the oxygen in this acid, is as 16 to 8, its *equivalent*, or combining proportion, is not 24, but 48, hence it must be considered as a compound of

Sulphur	2	32	66·67	=	Sulphur	1	16	33·33
Oxygen	2	16	33·33		Sulphurous acid	1	32	66·67
Hyposulphurous acid	1	48	100·00			1	48	100·00

HYPOSULPHURIC ACID (*Dithionic Acid*) (S_2O_5) was discovered by Gay-Lussac and Welther. It is obtained by passing a current of sulphurous acid through a cold mixture of finely-powdered and pure peroxide of manganese and water: $2SO_2+MnO_2=MnO,S_2O_5$. A solution is obtained, which is filtered and thoroughly agitated and digested with hydrated baryta, which must be added in small excess. The sulphuric acid and the greater part of the oxide of manganese are thus precipitated. The solution is again filtered and evaporated until it crystallizes, and the crystals of *hyposulphate of baryta* are a second time dissolved and obtained by evaporation, in order to procure them free from manganese; they are then dried, powdered, weighed, and dissolved in water; and to every hundred parts of the dissolved salt, 18·78 parts of sulphuric acid, of the specific gravity of 1·84, diluted with four parts of water, are added. The baryta is thus thrown down in the state of sulphate, and the new acid remains in solution. Having been filtered, it is to be concentrated by exposure under the exhausted receiver of an air-pump, including a vessel of sulphuric acid, until it acquires a density of 1·347. If the exposure and evaporation be continued beyond this point, it is resolved into sulphuric and sulphurous acids ($S_2O_5=SO_2+SO_3$). A temperature of 212° effects the same change in its composition. It is an inodorous acid, and reddens vegetable blues. It has not been obtained in an anhydrous state.

Hyposulphates.—These salts are remarkable for their solubility. When heated, they are resolved into sulphates, and sulphurous acid escapes. In the cold, sulphuric acid does not so act upon them as to set free sulphurous acid; but this acid is evolved on boiling. They do not give a deposit of sulphur when an acid is added to their solutions.

TRITHIONIC ACID (S_3O_5).—If three atoms of bisulphite of potassa in a saturated solution in water, are digested with two atoms of sulphur, hyposulphite and trithionate of potassa are produced, as in the following equation,

($3[KO,2SO_2]+2S=2[KOS_3O_5]+[KO,S_2O_2]$). The acid may be obtained from the trithionate by adding tartaric acid to the solution, but it soon undergoes decomposition. It gives no precipitate with the salts of baryta or lead. When a trithionate is heated, sulphur and sulphurous acid are given off, and a sulphate of the alkali remains.

TETRATHIONIC ACID (S_4O_5).—This acid was obtained by Fordos and Gélis (*Ann. de Ch. et Ph.*, Dec. 1842) by carefully decomposing its combination with baryta by sulphuric acid, so diluted as to avoid elevation of temperature. The tetrathionate of baryta may be procured by the reaction of iodine on hyposulphite of baryta $2(BaO,S_2O_2+I=BaI+BaO,S_4O_5)$. The diluted acid may be boiled without decomposition, but as it becomes concentrated, it deposits sulphur, evolves sulphurous acid, and the liquid contains sulphuric acid. The acid is not affected by dilute hydrochloric or sulphuric acids, but nitric acid throws down sulphur.

PENTATHIONIC ACID (S_5O_5).=This compound is produced by the reaction of sulphuretted hydrogen on a solution of sulphurous acid. Sulphur is deposited and the two preceding acids are simultaneously produced.

SULPHUR AND HYDROGEN. HYDROSULPHURIC ACID (HS). *Sulphydric acid. Sulphuretted Hydrogen Gas.*—This compound was discovered by Scheele in 1777. The two elements cannot be made to combine directly under ordinary circumstances; but when hydrogen is set free in the nascent state, in contact with a sulphur compound, this gas is immediately produced, and is recognized by its disagreeable odor. Sulphuretted hydrogen is thus evolved in the decomposition of many organic substances and in the action of water on the alkaline sulphides, on iron pyrites, as well as in the decomposition of water by heated coke containing sulphur.

Preparation.—Protosulphide of iron may be prepared by rubbing a roll of sulphur on a bar of wrought-iron heated to a full red heat, and collecting the compound as it melts in a pail of cold water. One part of this sulphide broken into small fragments may be placed in a retort with four or five parts of water and one part of sulphuric acid. The heat produced by the mixture of acid and water is sufficient to liberate the gas copiously. It is dissolved by water, and acts chemically upon mercury. It should be collected over a bath holding a small quantity of water, placed near to or under a flue. The chemical changes which ensue in its production, may be thus represented: $FeS+SO_3,HO=HS+FeO,SO_3$. The gas, as it is thus produced, generally contains a portion of free hydrogen. A mixture of sulphide of antimony and of hydrochloric acid also evolves, when heated, hydrosulphuric acid gas.

Properties.—Hydrosulphuric acid is a colorless gas at common temperatures and pressures. Under a pressure of about seventeen atmospheres at 50°, it assumes the liquid form: it is then limped, and apparently possessed of a refractive power exceeding that of water; its specific gravity is about 0·9. When a tube containing it was opened under water, it instantly and violently rushed forth under the form of gas (FARADAY, *Phil. Trans.*, 1823, p. 92.) When cooled to 122° below 0°, it solidifies, and it is then a white crystalline translucent substance, heavier than the liquid.

The gas has a peculiarly nauseous fetid odor, resembling that of rotten eggs, and so diffusible, that a single cubic inch escaping into the atmosphere of a large room, is soon perceptible by its smell in every part. 100 cubic inches weigh 36·38 grains. Its specific gravity compared with air is as 1·1747 to 1: and compared with hydrogen as 17 to 1. It is inflammable, burning with a pale blue flame, evolving the odor of burning sulphur. During its slow combustion, sulphur is deposited, and water and sulphurous acid are formed ($HS+O_3=SO_2+HO$). It extinguishes the flame of a taper. When respired, it proves fatal; and it is very deleterious, even though largely diluted with atmospheric air. Nausea, giddiness, headache, and a peculiar faintness, with loss of appetite, are the usual symptoms produced, when an atmosphere even slightly contaminated by sulphuretted hydrogen has been breathed for any length of time. When its escape into the laboratory cannot be prevented, its effects may be counteracted by the diffusion of a little chlorine, or by sprinkling the room with an aqueous solution of chlorine. The gas exists in some mineral waters, which are thence called sulphureous, such as those of Harrogate. It is also found in the air and water of foul sewers, and in putrescent animal matter.

Water dissolves three times its volume of this gas at 60°. The aqueous solution is transparent and colorless when recently prepared, but gradually becomes opalescent, and if exposed to air it deposits sulphur, while the hydrogen combines with the oxygen of air to form water. The whole of the gas is evolved by heat. It is an exceedingly delicate test of the presence of most of the metals, with which it forms colored precipitates. The colors of the sulphides produced, when accurately observed, serve to identify the respective metals. Thus arsenic and cadmium give a yellow, silver, lead, and bismuth a black, antimony an orange, and zinc a white sulphide. The symbols of the different metals may be printed on paper in the respective metallic solutions, and the paper exposed in a jar containing the gas. The colors produced by the different metals, are at once indicated by the symbols. One measure of sulphuretted hydrogen mixed with 200,000 measures of hydrogen, carburetted hydrogen, or atmospheric air, produces a sensible discoloration of white lead, mixed with water, and spread upon a piece of card, or on test-paper impregnated with a salt of lead. Cards which have been glazed with white lead are useful as a test for this gas. In this way we may ascertain the presence, in coal-gas or air, of extremely small quantities of sulphuretted hydrogen. The card or paper acquires a color varying from a pale brown to black, according to the quantity of the gas present in the mixture, or the length of exposure. The gas is entirely dissolved by a solution of potassa or ammonia.

Sulphuretted hydrogen reddens infusion of litmus and moist litmus-paper; it is generally classed among the hydracids, and is not, therefore, considered to unite directly with the basic oxides, a metallic sulphide and water being the usual results of their mutual reaction ($HS,MO=MS,HO$); it combines certain sulphides (basic sulphides), and forms a class of *sulphur salts;* compounds which are analogous to the hydrated oxides, if we substitute sulphur for oxygen.

When hydrogen becomes sulphuretted hydrogen, its volume is unchanged: and when one volume of sulphuretted hydrogen is detonated with half its volume of oxygen, water is formed and sulphur is precipitated ($HS+O=HO+S$), the whole of the mixed gases being condensed. But when a volume of sulphuretted hydrogen and a volume and a half of oxygen are inflamed in a detonating tube, one volume of sulphurous acid is produced, and water is condensed. Thus the sulphur is transferred to one volume of the oxygen, and the hydrogen to the half volume. This gas, therefore, consists of its volume of hydrogen plus one-sixth of its volume of sulphur, or 16 parts by weight.

	Atoms.	Weights.	Per cent.	Vols.	Sp. Gr.
Sulphur	1	16	94·1	$\frac{1}{6}$	1·1056
Hydrogen	1	1	5.9	1	0·0691
Sulphuretted hydrogen .	1	17	100·0	1·00	1·1747

It will be observed that this compound differs from the other hydracid gases in undergoing condensation: hence its atomic volume, which is always equal to the hydrogen present, is represented by 1. The hydrochloric, hydriodic, and hydrobromic acids have an atomic volume represented by 2, the hydrogen being equal to only one-half of the volume of the gas. Whether sulphur be considered as representing one-sixth, one-third, or a whole volume of vapor, the result is the same; it adds nothing to the volume of this gas. In constitution this gas resembles water, if we suppose sulphur to be substituted for oxygen, rather than the hydracid gases of the halogenous elements. When a current of the gas is heated to full redness in a glass tube, it is decomposed, and sulphur is deposited. Spongy platinum does not effect the combustion of a mixture of sulphuretted hydrogen and oxygen unless free hydrogen be also present.

Chlorine, iodine, and bromine, in vapor, instantly decompose hydrosulphuric acid gas; when they are not in excess, sulphur is deposited, and hydrochloric, hydriodic, and hydrobromic acids are formed. Strong nitric acid poured into the gas occasions a deposition of sulphur, and nitrous acid and water are formed, with a considerable elevation of temperature, and occasionally flame. A fold of bibulous paper dipped in the acid may be safely introduced. An aqueous solution of the gas is also decomposed by these reagents. When two volumes of this gas are mixed in an exhausted vessel with one of sulphurous acid, they mutually decompose each other, occasioning the production of water, and the deposition of sulphur ($2HS+SO_2=2HO+3S$). If the gases are perfectly dry, the action is slow. Strong sulphuric acid also decomposes hydrosulphuric acid; the results are water, sulphurous acid, and sulphur ($HS+SO_3=HO+SO_2+S$): but if the acid be diluted with four or five parts of water, it has no action, and if in that case it is rendered turbid by the gas, the presence of sulphurous or arsenious acid may be suspected. Hydrosulphuric acid decomposes chromic as well as iodic acid, and in the latter case sets free iodine. Sulphur is in these cases precipitated. Hydrochloric acid has no action on it. It is completely oxidized and the odor is removed by an alkaline permanganate. Chloride of zinc decomposes it, and sulphide of zinc is formed. The gas is rapidly absorbed by charcoal, the hydrogen is oxidized and sulphur is deposited. If a weak solution of sulphuretted hydrogen is shaken with powdered charcoal, the smell of the gas rapidly disappears, and on filtering the liquid it no longer acquires a brown color by the addition of a salt of lead. Owing to this property, Dr. Stenhouse has recommended the use of a charcoal-respirator for persons who may breathe the exhalations of sewers.

One of the most efficient metallic compounds for the removal of sulphuretted hydrogen either in the gaseous or dissolved form, is the hydrated peroxide of iron. The substance is now largely employed for the separation of sulphuretted hydrogen from coal-gas. Black sulphide of iron and water are formed, and sulphur is set free ($Fe_2O_3+3HS=3HO+FeS+S$). The change takes place on contact, but more rapidly when aided by heat and moisture. The sulphide of iron is reconverted into oxide on exposure to air [$2FeS+O_3(\text{air})=Fe_2O_3+S_2$]. This fact illustrates the facility with which sulphur and oxygen may replace each other in metallic combinations.

When potassium or sodium is heated in hydrosulphuric acid gas, a sulphur-salt of the metal is formed with vivid combustion, and pure hydrogen is liberated ($K+2HS=KS,HS+H$). When tin or lead is heated in the gas, they also decompose it, and absorb the sulphur, leaving a volume of hydrogen equal to that of the original gas. Passed over metallic oxides, water and metallic sulphides are the results: the different oxides effect this decomposition at very different temperatures.

Tests.—1. The odor of the gas is sufficient to reveal its presence, even when it forms only 1-200,000th part of the atmosphere. 2. Paper wetted with a solution of acetate of lead and dried, or a glazed card, will indicate, by the appearance of a brown color, the presence of the gas, even when the proportion is infinitesimal. The same tests apply to the presence of sulphuretted hydrogen in water. In addition, a portion of leaf-silver may be allowed to remain in the water for some hours. If the gas is present, the silver will be sooner or later tarnished.

Persulphide of Hydrogen.—This is a liquid compound, the composition of which is not accurately known, but it is supposed to be HS_5. It is procured by adding a solution of persulphide of calcium to diluted hydrochloric acid. Under these circumstances, sulphuretted hydrogen is not produced, but the greater part of the sulphur remains united to it, producing a heavy yellow liquid, which subsides to the bottom of the glass. It has a sp. gr. of 1·76; it is inflammable, and is rapidly decomposed in water or by exposure to air.

Sulphide of Ammonium (NH_4S).—As ammonia is not a metallic oxide, it is assumed that when hydrosulphuric acid meets with this alkaline gas, the hydrogen is at once transferred to the ammonia, producing ammonium, with which the sulphur remains combined. If the dry gases are placed in contact, a volatile anhydrous crystalline compound is produced, which has the composition NH_3+2HS, or, as it is frequently represented, NH_4S+HS. The crystals are soluble in water. The sulphide of ammonium, commonly used as a test, is really the hydrosulphate of the sulphide, and has the composition above given. The ordinary solution is made by saturating with sulphuretted hydrogen one-half of a measured quantity of a solution of ammonia, and then adding to it the other half. At first the liquid is pale, but after some time, and as a result of exposure to air, it acquires a deep yellow color, owing to the liberation of sulphur and the production of bisulphide of ammonium (NH_4S_2). A portion of the hydrogen combines with the oxygen of the air. It is ultimately converted into hyposulphite of ammonia, and sulphur is precipitated. If the solution of sulphide is properly prepared, it should give no precipitate with a solution of sulphate of magnesia. The liquid, when concentrated, evolves an irritating vapor, which is strongly alkaline, and has a very offensive odor. It is a convenient test for the precipitation of numerous metals as sulphides. With some of these it enters into combination, forming double sulphides.

Persulphide of Ammonium.—This is a compound of sulphuretted hydrogen and ammonia, with excess of sulphur. It is probably a bisulphide. It is obtained by distilling a mixture of about 4 parts of slaked lime, 2 of hydrochlorate of ammonia, and 1 of sulphur. In its concentrated state, this compound exhales white fumes; hence it was formerly called *Boyle's fuming liquor.* It is a deep yellow liquid, smelling like a mixture of sulphuretted hydrogen and ammonia. It dissolves sulphur.

Sulphides.—The soluble monosulphides are easily recognized: 1. By the odor of sulphuretted hydrogen when wetted, or when an acid is added. 2. In solution, by the deep brown or black precipitate, which is produced on adding a salt of lead. 3. By the rich purple or crimson color produced on the addition of a few drops of a fresh solution of nitroprusside of sodium. The color produced in this reaction, is of a blue or splendid purple tint, when the alkaline sulphide is in small quantity, and of a rich crimson, in stronger solutions. The color is slow in appearing in a weak solution of sulphide, and sooner or later fades. As the nitro-prusside produces no change of color, in a solution of sulphuretted hydrogen, this reaction enables a chemist to say whether the solution is or is not mixed with any traces of sulphide. The monosulphides may be represented by MS, the sulphuretted sulphides by MS,HS, and a polysulphide by MS_5. Solutions of pure monosulphides are pale, and evolve sulphuretted hydrogen without yielding a precipitate of sulphur, when hydrochloric acid is added to them. Solutions of persulphides have a deep orange or amber color, and when treated with an acid, not only evolve sulphuretted hydrogen, but give an abundant precipitate of sulphur of a pale lemon-white color (*precipitated sulphur*).

Chloride of Sulphur (SCl).—When sulphur is heated in an excess of dry chlorine, it absorbs rather more than twice its weight of this gas. Ten grains of sulphur absorb 30 cubic inches of chlorine, and produce a liquid of a greenish-yellow color by transmitted light, but orange-red by reflected light. The combination also takes place at common temperatures, and may be effected by passing an excess of dry chlorine through a tube containing powdered sulphur. Chloride of sulphur exhales suffocating and irritating fumes when exposed to the air. Its specific gravity is 1·60. It boils at 146°, yielding a vapor of the density of 3·70.

Dichloride of Sulphur; Subchloride of Sulphur (S_2Cl).—When the preceding liquid is saturated with sulphur, it deposits a portion, often in crystals, but retains an additional atom of sulphur, forming a yellow-brown liquid of the specific gravity of 1·686. It boils at 282°. The density of its vapor is 4·70. It is a powerful solvent of sulphur, and is used in the cold vulcanization of caoutchouc. It also dissolves phosphorus. Tetrahedral crystals of sulphur may be obtained from this liquid, the deposition of which is much influenced by light. According to Rose (*Poggendorff's Ann.*, xxxi.), this is the only chloride of sulphur, and the preceding compound is merely a solution of chlorine in this dichloride. When dropped into water, it gradually yields hydrochloric acid, sulphur, and hyposulphurous acid, the latter resolving itself into sulphurous acid and sulphur: $2S_2Cl,2HO=2HCl,SO_2,3S$.

Sulphur forms compounds with bromine, SBr; with iodine, SI; and nitrogen, S_2N; but these present no features of interest.

Selenium (Se=40).

Selenium was discovered in 1817 by Berzelius, during an examination of certain substances, found in the sulphuric acid, manufactured at Gripsolm, in Sweden. (*Ann. Ch. et Ph.*, ix. 160.) The sulphur used in these works is procured from the iron pyrites of Fahlun, and the acid obtained from it deposits a red matter, which was supposed to contain tellurium, but which was proved to be a distinct substance, to which its discoverer gave the name of *Selenium*, from *σελήνη, the moon.* It resembles sulphur, and is generally placed next to it among the non-metallic bodies.

Preparation.—Selenium may be obtained by the decomposition of selenic acid, which may be effected by adding hydrochloric acid to its solution in water, and immersing a plate of zinc in the mixture: a gray or reddish-brown flocculent precipitate of selenium is then deposited. Selenium may also be extracted from the native sulphide of iron which contains it, by mixing the powdered sulphide with eight parts of peroxide of manganese, and exposing the mixture to a low red heat in a glass retort, the beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid gas, while the selenium is either sublimed in vapor or in the state of selenious acid: should any of the latter go over into the water it would there be reduced to selenium by the sulphurous acid.

Properties.—Selenium, when cooled after fusion, has a reddish-brown color, and a dim metallic lustre; it is very brittle and its fracture is of a lead-gray color. Its specific gravity is 4·32. Specific heat=0·0837. Obtained from its solutions by precipitation upon zinc, it is red, but becomes black when boiled in water. It has neither taste nor smell. When fused, and very slowly cooled, its surface is granular, without lustre; and its fracture dull, like that of metallic cobalt. It is easily reduced to a powder, which is red. It is a non-conductor of heat and electricity. Selenium is softened by heat, becoming semifluid at 212°, and melting at a temperature somewhat higher; it remains for some time soft on cooling, and may be drawn out into filaments like sealing-wax, which are of a gray metallic lustre by reflected light, but by transmitted light of a clear ruby-red. Heated in a tube to about 650°, it boils, and is converted into a yellow vapor, which condenses into black drops that run together like quicksilver. It is entirely volatile. It does not, like sulphur, assume a crystalline state on cooling. Heated in the open air it rises into vapor, which may be condensed into a red powder. It is characterized by tinging flame of a light-blue color, and by exhaling, when strongly heated, a peculiarly offensive odor. It is combustible, but when ignited it does not continue to burn, like sulphur. It evolves no acid vapor resembling sulphurous acid. It is insoluble in water, and scarcely dissolved by benzole, except at the boiling-point. Its best solvent is boiling sulphide of carbon, but it is taken up in very small proportion, and is left as a red powder by spontaneous evaporation. Powdered selenium when heated in liquids, even in solutions of alkalies, has a tendency to agglutinate, forming a mass which the solvent scarcely attacks. Selenium is considered to exist in two different states—the one vitrous and the other metallic-looking. The vitreous condition is obtained by the slow cooling of the melted substance. In this allotropic state, it is insoluble in sulphide of carbon, while in the other form, it is soluble.

When sulphur is mixed with selenium, they may be separated by deflagrating the mixture with nitrate and carbonate of potash. Sulphate and seleniate of potassa are obtained, which may be separated by the process described under *Seleniates.*

Assuming the combining volume of the vapor of selenium to be the same as that of sulphur, and that one volume of selenious acid includes one volume of oxygen, and one-sixth of a volume of selenium vapor, then the density of the latter would be by calculation 16·6392 (air=1), and compared with hydrogen 240; 100 cubic inches would weigh 515·8 grains. Selenium forms three compounds with oxygen—one oxide and two acids. These compounds are thus constituted:—

	Oxide (SeO).	Selenious Acid (SeO_2).	Selenic Acid (SeO_3).
Selenium	83·33	71·06	62·07
Oxygen	16·67	28·94	37·93

This body differs from sulphur in forming an oxide.

Oxide of Selenium (SeO) is formed by heating selenium in a limited quantity of atmospheric air, and washing the product to separate a portion of acid which is at the same time formed. The oxide is sparingly soluble in water, but it does not redden litmus or combine with alkalies. It appears to be the source of the peculiar odor, emitted during the oxidation of selenium.

Selenious Acid (SeO_2).—This acid may be obtained in a solid state by digesting selenium in nitric or nitrohydrochloric acid until entirely dissolved, and then evaporating to dryness. Its taste is sour and hot: its odor, when sublimed, acrid, but not like that of the oxide. It is very soluble in warm water, and the solution furnishes crystals of the hydrated acid. The selenious acid and its salts are decomposed by sulphurous acid—selenium being slowly separated in red flocculi ($SeO_2+2SO_2=Se+2SO_3$).

SELENIC ACID (SeO_3).—This acid is obtained by fusing selenium or selenious acid, or any of its salts, with nitrate of potassa or soda; an alkaline seleniate is thus obtained. This may be dissolved in water and decomposed by nitrate of lead. The insoluble seleniate of lead thus obtained, is diffused through water, into which a current of sulphuretted hydrogen is passed to precipitate the lead; the liquid is boiled, to expel any excess of sulphuretted hydrogen, and is now diluted selenic acid; it may be concentrated by careful evaporation, but the acid cannot be entirely deprived of water without being decomposed.

Selenic acid as thus procured, is a colorless liquid, which may be heated to about 536° without change; but it is partially decomposed at higher temperatures; and at 554°, is rapidly resolved into selenious acid and oxygen ($SeO_3 = SeO_2 + O$). When concentrated, by exposure to a temperature of about 329°, it acquires a specific gravity of 2·524; at 513°, it is 2·6: it may be rendered somewhat denser by exposing it to a higher temperature; but in this case a portion of selenious acid is formed in it. It is unknown in an anhydrous state. The hydrated acid may be represented by HO,SeO_3. When boiled with hydrochloric acid, selenious acid and chlorine are produced, so that the selenio-hydrochloric acid dissolves gold like the nitro-hydrochloric ($HO,SeO_3 + HCl = HO,SeO_2 + HO + Cl$). It dissolves zinc and iron with the evolution of hydrogen; and copper, with the production of selenious acid. Sulphurous acid, which decomposes selenious acid, has no action on selenic acid; so that to decompose selenic acid, it must first be boiled with hydrochloric acid, which converts it into selenious acid; and sulphurous acid, or a sulphite, then effects the separation of selenium. The affinity of selenic acid for bases is little inferior to that of sulphuric acid.

Seleniates:—The selenic and sulphuric acids are isomorphous, as are the seleniates and sulphates, as well as the chromates and manganates. The seleniates mostly withstand a red heat: they are more easily reduced at high temperatures by hydrogen, than the sulphates. Heated with sal-ammoniac, they are decomposed with the separation of selenium. The seleniates of baryta, strontia, and lead, are insoluble in water, and in dilute nitric acid. A seleniate boiled with hydrochloric acid dissolves gold. It is thus distinguished from a sulphate. When a sulphate is mixed with a seleniate, they may be separated by passing into the solution after boiling it with hydrochloric acid, a current of sulphurous acid gas. Selenium is thrown down in red flocculi, while the alkaline sulphate remains in the solution.

SELENIURETTED HYDROGEN; HYDROSELENIC ACID (HSe).—This is a colorless gaseous compound which may be obtained by the action of hydrochloric acid upon selenide of potassium or of iron. It is readily dissolved by water, forming a solution at first colorless, but after a time acquiring a reddish hue; the solution smells and tastes somewhat like that of sulphuretted hydrogen; it reddens litmus, and tinges the skin of a reddish-brown color. Nitric acid dropped into it occasions no change, and the gas does not readily escape from the water; but, when exposed to air, the solution is gradually reddened, and deposits selenium, the hydrogen combining with the oxygen of air. It occasions black or dark brown precipitates in all solutions of neutral metallic salts, with the exception of those of zinc, manganese, and cerium, which are flesh-colored. Heated with tin, one volume yields one volume of hydrogen and selenide of tin. It is decomposed by the joint action of air and water; it is absorbed by moist substances, and soon communicates to them a red color. The selenium is thus remarkably deposited throughout the texture of organic bodies. A piece of moist paper is penetrated by the red color. It exerts a noxious action upon the trachea and organs of respiration; it inflames the eyes, and painfully stimulates the nasal membrane, destroying for some hours the sense of smell. The gas is inflammable. By combustion it produces water, and in close vessels leaves a reddish-colored deposit of selenium.

The specific gravity of seleniuretted hydrogen is 2·795. It contains one volume of hydrogen and one-sixth of a volume of selenium condensed into one volume of the compound. Its equivalent or atomic weight is 41. The gas contains 97·52 per cent. of selenium. Although considered to be a hydracid gas, it shares the peculiarity of hydrosulphuric acid. Its atomic volume is equal to the amount of hydrogen, and is not affected by the large amount of the metalloid which enters into combination with it. Two volumes of this gas contain two of hydrogen, but two volumes of hydrochloric acid contain only one of hydrogen.

CHAPTER XVIII.

PHOSPHORUS (P=32). ITS COMPOUNDS WITH OXYGEN AND HYDROGEN.

History.—Phosphorus, so termed from its property of shining in the dark, (from φῶς, *light*, and φέρειν *to bear*,) occurs in the three kingdoms of nature, but most abundantly as a component of the bones and urine of animals: it is generally present as phosphoric acid, combined with various bases. Although phosphorus is found in certain phosphates in the mineral kingdom, it is, like carbon and sulphur, a most important constituent of organic matter. It exists in albumen, fibrin, and gelatine, in the brain, blood, milk, and other secretions. It is found in combination with oxygen, united to lime and magnesia, in the seeds and husks of the cerealia, and in numerous esculent roots. There is no substance which yields it so abundantly as bone. The subphosphate of lime forms about eighty per cent. of calcined bone, and from this source it is now exclusively obtained.

Phosphorus was discovered in 1669, by Brandt, a merchant of Hamburg, in the solid residue of urine, but no practical use was made of the discovery until a century later, when a process for preparing this substance from bone, was first made public by Scheele and Gahn.

Preparation.—On twenty parts of calcined bone, ground to a fine powder, pour forty of water (by weight) and eight parts of sulphuric acid, previously diluted with an equal weight of water. These materials are well stirred together by means of a revolving wooden stirrer, for about six hours, steam being let into the mixture to promote the chemical changes. The whole is then put into a conical bag of linen to separate the clear liquor, and the residuum is washed and pressed until the water ceases to taste acid. Evaporate the strained liquor, and when reduced to about half its bulk, let it cool. A white sediment will form, which must be allowed to subside; the clear solution (superphosphate of lime) must be decanted and boiled to dryness in a glass vessel. A white mass will remain, which may be fused in a platinum crucible, and poured out into a clean copper dish. A transparent substance is thus obtained, consisting of phosphoric acid, with phosphate, and a little sulphate of lime, commonly known under the name of *glass of* *phosphorus.* It yields phosphorus when distilled at a white heat with one-fourth of its weight of charcoal. The retort, which is made of the most refractory fire-clay, should be well and carefully luted, and should have a wide neck terminating in a copper tube, so bent as to dip perpendicularly into a bottle of hot water, otherwise it is apt to become plugged up by congealed phosphorus. When cold, it is cut into small pieces, which are put, with water, into a slightly conical glass tube, and fused by immersion in hot water: on cooling, the phosphorus is withdrawn in the shape of a stick.

The changes which take place in the various stages of this process, may be thus described. The subphosphate of lime in bone is $3(CaO),PO_5$. Sulphuric acid transforms this salt into acid phosphate (superphosphate) and sulphate of lime, $3(CaO)PO_5+2SO_3=CaO,2(HO)PO_5+2(CaO,SO_3)$. The acid phosphate when heated with charcoal is converted into pyrophosphate (which is not decomposed by carbon) carbonic oxide and phosphorus, a portion of the phosphoric acid being set free and deoxidized by the charcoal at a white heat, $2(CaO,PO_5)+C_5=5CO+2(CaO)PO_5+P$. Phosphuretted hydrogen also escapes during the process as a result of the reaction of the vapor of phosphorus on water.

The phosphorus obtained by the first distillation is commonly of a dirty red or brown color, owing to the presence of impurities. It is melted in a solution of ammonia, and is bleached by heating it in a mixture of bichromate of potassa and sulphuric acid. After this it is again melted, and while liquid is strained through chamois-leather. The mechanical impurities are thus separated, and it is recast into sticks in the manner above described. This substance is now manufactured in tons, chiefly for the purpose of making lucifer matches. According to Mr. Gore, about six tons are annually consumed in Great Britain in the match manufacture—and one pound will suffice for 600,000 matches. This manufacture is, however, conducted on a larger scale abroad. There are two manufactories on the continent, which consume twenty tons of phosphorus annually.

Properties.—When pure, solid phosphorus is tasteless, but when in solution, it has a sharp nauseous taste: it is colorless, or of a pale yellow color, translucent, sectile, and flexible at common temperatures, but at 32° vitreous and brittle. Exposed to air, it exhales luminous fumes, having a peculiar odor, distantly resembling that of garlic, and ozone is produced (*see* page 101). Its specific gravity is 1·826 at 50°. Its specific heat is 0·1887 (REGNAULT). It is a non-conductor of electricity, both in its solid and fluid state. Phosphorus is insoluble in water, but it is dissolved sparingly by absolute alcohol, ether, the oils, naphtha, benzole (and other liquid hydrocarbons), but most abundantly by sulphide of carbon. The chlorides of sulphur and of phosphorus also dissolve it. When water is added to the alcoholic solution, phosphorus is separated as a milk-white substance, probably in the state of hydrate. If the alcoholic solution be poured on hot water in the dark, there is an evolution of light arising from the slow combustion of phosphorus. The solution in ether presents similar phenomena. If this be rubbed over the skin or any warm surface, in the dark, the luminosity of phosphorus is seen in a pale, bluish-colored, lambent flame, which produces no sense of warmth. The ethereal solution is decomposed by exposure to light, and red oxide of phosphorus or red phosphorus is deposited. The saturated solution in sulphide of carbon, if allowed to evaporate spontaneously on paper, leaves a finely divided residue of phosphorus, which, when dry, instantly takes fire, and burns in air with a brilliant white light peculiar to this body. Although phosphorus is not soluble in water, it is slowly oxidized in this liquid, which is soon found to acquire an acid reaction, and to have the mixed properties of phosphorous and phosphoric acids. As no hydrogen escapes, it is probable that the air diffused through the water, furnishes oxygen. Under exposure to light, phosphorus acquires a reddish color. This was supposed to be caused by oxidation, but as it takes place *in vacuo* it is probably owing to a molecular change in phosphorus itself, a superficial layer of the metalloid being changed into amorphous phosphorus. The white layer which forms on the surface, when phosphorus is kept in the dark, has been also ascribed to molecular changes. The phosphorus in which this change has taken place is very fusible and inflammable.

Phosphorus cannot be readily crystallized by fusion; it passes too slowly from the liquid to the solid state, but it may be crystallized by solution. By slowly cooling some of its hot saturated solutions, phosphorus has been procured in crystals, having the form of rhombic dodecahedra. Crystals of this substance have also been obtained, by melting under water two parts of phosphorus to one of sulphur: a portion of the phosphorus is deposited in regular crystals on cooling. (*See Sulphide of Phosphorus.*) When air is excluded, phosphorus melts at about 110°, undergoing an increase of volume. If suddenly cooled to 32°, after having been heated to 140°, it sometimes becomes black (THENARD); but if slowly cooled, it remains colorless. When fused and left undisturbed, it may remain liquid for hours at the usual temperature, particularly when covered by an alkaline liquid. At from 550° to 570° in close vessels, it boils and evaporates in the form of a colorless vapor, the density of which, according to Dumas, is 4·355; 4·326 (REGNAULT); 100 c. i. weigh 136·96 grains. But phosphorus evaporates, especially if in contact with moisture, at a much lower temperature. The volatility of phosphorus in conjunction with aqueous vapor, may be shown by boiling a flask of water containing a piece of phosphorus, over a lamp; the vapor, as it issues from the flask, is luminous in a dark room. Owing to its great inflammability, it should always be preserved in water, in a dark place, and, when required, cut under water.

Phosphorus is a formidable poison; a few grains of this substance are sufficient to destroy life. Even the vapors when breathed (as in lucifer-match making) produce caries and necrosis of the jaws, with wasting disease.

There are some peculiar circumstances connected with the luminosity and inflammability of phosphorus. When exposed to humid air at temperatures above the freezing-point, it shines in the dark with a pale blue light, which increases in intensity with the temperature. This arises from slow combustion, attended by the production of phosphorous acid (PO_3) and ozone. If a streak is drawn on litmus-paper with a stick of dry phosphorus, the paper is slowly reddened. The luminosity ceases in close vessels as soon as the oxygen has been absorbed, and it does not take place when the air has been artificially dried: in this case the formation of phosphorous acid seems to be prevented. In pure oxygen, phosphorus is not luminous until heated to between 70° and 80°, above which temperature it becomes strongly luminous, and soon inflames. Gases, in which phosphorus has been immersed, acquire its odor, and when mixed with air, they become slightly luminous. If a piece of phosphorus be introduced into a vessel of pure and dry oxygen gas over mercury, at a temperature not exceeding 80°, no perceptible absorption will happen in twenty-four hours; but if, the temperature remaining the same, the pressure be diminished to one-eighth or one-tenth of that of the atmosphere, the phosphorus will be surrounded with white vapors, will become luminous in the dark, and will absorb oxygen. Graham has shown that the slow combustion of phosphorus in air is prevented by small additions of certain gases and vapors. Thus at the temperature of 66°, and even above this, oxidation is entirely prevented by the presence of small quantities of sulphurous acid, sulphuretted hydrogen, and of olefiant gas, as well as by the vapors of sulphide of carbon, ether, creasote, naphtha, and oil of turpentine. This is probably owing to the oxidation of these vapors, since it has been noticed that when two oxidable bodies are in contact, one of them often takes precedence in combining with oxygen, to the entire exclusion of the other. Potassium is defended from oxidation in air by the same vapors, though to a less degree. When these oxidable vapors are absent, there is no better test of the presence of free oxygen, than that furnished by the luminosity of phosphorus in the dark.

When a piece of dry phosphorus is sprinkled with lamp-black, or powdered animal charcoal, it is apt to inflame; and, what is curious, when very thin slices of dry phosphorus are placed upon dry wood, flannel, wool, lint, fine feathers, or other non-conducting substances, they speedily fuse and readily inflame upon the gentlest friction. It seems as if the slow combustion of the phosphorus, produced heat enough to fuse it whilst lying upon a very bad conductor. If several pieces of phosphorus be placed upon or near to each other, they are also apt to inflame.

The actual temperature at which phosphorus inflames has been variously stated; but it is generally a little above its melting point. We have noticed that phosphorus coated with a white layer, has melted below 70°, and burst into flame on being touched. Phosphorus easily takes fire by the heat of the hand and by slight friction, as when rubbed upon a piece of coarse paper: it requires, therefore, to be handled with the utmost caution. Owing to the superficial formation of phosphorous and phosphoric acids, when it burns imperfectly at low temperatures, its further combustion is often prevented: thus, in rubbing a fragment of phosphorus between two pieces of brown paper, a momentary combustion ensues, and it often requires considerable friction to cause it again to inflame. For the same reason it is difficult to light a piece of paper by the flame of phosphorus, the paper becoming covered and protected by the acid produced. So also a small piece of phosphorus may be fused by the gradual application of heat, but it will not inflame until the surface is disturbed by touching it with a wire. A fragment gently heated on writing-paper, may be melted and consumed without igniting the paper. Paper or linen soaked in phosphate of ammonia, is, for a similar reason, rendered uninflammable by the application of heat; ammonia is volatilized, and the phosphoric acid liberated, glazes over and protects the material from combustion.

When in brilliant combustion in the air, phosphorus evolves copious fumes of phosphoric acid (PO_5): its flame is intensely luminous, and nearly white. If phosphorus be heated in a confined portion of air, it enters into less perfect combustion, and an oxide, a red solid, less fusible than phosphorus, is produced. The different products of the combustion of phosphorus are well shown by heating a fragment of it placed near the centre of a thin glass tube of about a fourth of an inch diameter, and three or four feet long, and then gently driving a current of air through the tube; the fixed and volatile acids, and the red oxide, are in this way distinctly separated.

The vapor of phosphorus explodes with oxygen, and burns violently where it meets with air. It may be safely produced and burnt at the mouth of a test-tube, by heating a piece of phosphorus in a small quantity of ether. The tube becomes filled with ether-vapor, and the phosphorus-vapor burns only as it issues from the mouth of the tube. Gases in which oxygen is in a combined state, do not readily part with it to phosphorus, even at the temperature of combustion. Thus burning phosphorus is extinguished in pure carbonic acid. It may be melted in deutoxide of nitrogen by a heated wire without being inflamed; but when introduced into this gas in a boiling state, it decomposes it, and unites to the oxygen, producing a vivid combustion. It takes fire spontaneously in chlorine, burning with a pale flame; and on contact with iodine, the heat of combination is such as to kindle the phosphorus immediately.

Its great affinity for oxygen is manifested not only by its luminosity in air at a low temperature, but by its decomposition of the oxides of certain metallic salts. Small portions of fresh-cut phosphorus suspended in weak solutions of sulphate of copper, nitrate of silver, chloride of gold, and chloride of platinum, are speedily coated with layers of the respective metals, sometimes deposited in a beautifully crystalline state. Phosphorus here acts as a powerful deoxidizer, and is converted into phosphoric acid ($P+5(AgO, NO_5)=5Ag+PO_5+5NO_5$, and $5\,(CuO, SO_3)+P=5Cu+PO_5+5SO_3$). If some thin slices of phosphorus be placed on a very diluted solution of chloride of gold (a grain of chloride to 4000 of water), and covered over, they will soon be surrounded by thin transparent films of reduced gold, which may be raised from the fluid by clean and dry plates of glass. There is no instance in which metallic gold is brought to a finer state of tenuity than in this experiment. Advantage is taken of this property in the electrotype art, for coating vegetable and animal substances, insects, seeds, &c., with a layer of metal, and thus making them conductors. The substance is brushed over with a small quantity of a weak solution of any salt of gold, silver, or platinum, and it is then exposed to the vapor of a solution of phosphorus in alcohol or ether. A thin film of metal is deposited, and this serves as a conducting surface for a further deposit by the battery. An alcoholic solution of phosphorus throws down the metals from solutions of gold and silver. Phosphorus decomposes solid nitrate of silver and chlorate of potassa with a violent explosion, when a mixture of the two substances is suddenly struck with a hammer.

Equivalent.—The atomic weight of phosphorus is in round numbers 32. As the specific gravity of its vapor, compared with hydrogen is 63·71, it follows that its atomic volume must be 0·5, or half a volume, so that each volume of vapor, like that of oxygen, will necessarily contain two atoms. (*See* p. 66.) It is diatomic. The hypothesis of Gerhardt, that the atomic weights of elements in the gaseous or vaporous condition, correspond to single volumes of their vapors, is therefore wholly inconsistent with the facts which are known regarding the vapor of phosphorus. Deville did not find that a heat of 1900° in any way affected the relative volumes or the specific gravities of phosphorus and oxygen.

Tests.—The smallest fragment of phosphorus, even when mixed with other substances, may be sometimes identified by its garlic odor, and in all cases by its luminosity in the dark. If the substance suspected to contain phosphorus, is dried and heated in the dark, in a thin layer spread on a metallic plate, the minutest fragments of phosphorus will appear luminous, or will burn with a puff of white vapor. The contents of the stomach and intestines of persons poisoned by phosphorus have been, in some instances, quite luminous in the dark. If the test of luminosity should fail under these circumstances, the dried substance should be digested in its volume of sulphide of carbon for twenty-four hours. The liquid strained off should be poured into a watch-glass, floating on a surface of hot water in the dark, when, if phosphorus be present, there will be a luminosity, as the sulphide evaporates.

Allotropic, or *Amorphous Phosphorus.*—It has been already remarked that phosphorus, when suddenly cooled from a state of fusion, undergoes certain changes in its physical properties. As a result of exposure to heat or light, it acquires a red color, and this red substance, which is allotropic or amorphous phosphorus, is possessed of peculiar properties, which have been fully described by Schrötter and others. (*Ann. Ch. et Ph.* 3eme Sér., 24, p. 406.) Schrötter made the discovery of this variety of phosphorus in 1848. He obtained it by distilling phosphorus in an atmosphere of nitrogen or carbonic acid, at a temperature between 460° and 480°. In this case, a part of the phosphorus assumes the amorphous or red condition, while the unchanged portion acquires the property, after repeated distillations, of remaining for a long time liquid, and even sustaining considerable agitation without congealing. To separate the common, from the amorphous kind, sulphide of carbon is employed. This dissolves common phosphorus only, and leaves the allotropic variety, after having been well purified by washing with the sulphide, in the form of a red or brownish-red powder. For commercial purposes, allotropic phosphorus is made by heating phosphorus under water, in an air-tight cast-iron boiler to a temperature of 450°. A quantity of about 200 pounds of ordinary phosphorus is thus kept heated, for three or four weeks. When the vessel is opened, the phosphorus presents itself as a hard, red, brick-like-looking substance, as brittle as glass. It is broken into small pieces under water, and ground between mill-stones in a vessel supplied with a small stream of water, which washes the finer particles into a tank, in which they subside. Any unchanged phosphorus is then removed by sulphide of carbon. (GORE.) For the purpose of experiment, this change may be shown by heating a small portion of phosphorus to a proper temperature, in a tube filled with dry carbonic acid gas. The change of color produced by heat, and the volatility of phosphorus at a still higher temperature, may thus be proved. One end of the tube should be sealed, and the other end should be plunged into mercury or water.

Properties.—The color of amorphous phosphorus varies, according to the temperature to which it has been exposed, from nearly black (with a metallic lustre) to iron-gray, brick-red, crimson, and scarlet. It has no odor. Its specific gravity at 50° is 1·964 to 2·14. When dry, it undergoes no change in air: when moist it is slowly oxidized, but it is not luminous in the dark, and it produces no ozone. It does not remove oxygen from air, and will not combine with this gas to produce the phenomena of combustion under a temperature of 500°; but it requires to be heated to 570° for its entire combustion. In vessels filled with carbonic acid or nitrogen, it may be distilled over as ordinary phosphorus at this temperature. Chlorine acts upon it, producing heat, but no evolution of light. Chloride of phosphorus is formed. Iodine has no action upon it; and although it is only phosphorus in an altered molecular condition, it has no poisonous properties. In addition to the characters above described, allotropic phosphorus is quite opaque, hard, and brittle, and without crystalline structure. It is insoluble in sulphide of carbon, ether, and all the liquids which dissolve common phosphorus. It is slightly dissolved by a solution of chlorine. Although it is considered to be less energetic in its affinities than common phosphorus, yet when mixed in equal parts with chlorate of potassa, it explodes with tremendous violence, and with the slightest friction.

From this description it will be perceived that although the two varieties are easily convertible into each other, they differ as much in properties as any two metalloids, or metals. The amorphous phosphorus has not yet been successfully employed for the manufacture of lucifer-matches.

PHOSPHORUS AND OXYGEN.—Phosphorus combines with oxygen to form four different compounds:—

Oxide of phosphorus . . .	P_2O	Phosphorous acid . . .	PO_3
Hypophosphorous acid . .	$P\,O$	Phosphoric acid . . .	PO_5

OXIDE OF PHOSPHORUS (P_2O).—When phosphorus is burnt in air, there is generally a red residue, which consists in great part of this oxide. If a large quantity of phosphorus is burned in a confined volume of air, the oxide is abundantly produced. It may be prepared in quantity, by melting phosphorus in a conical glass under hot water, and then passing upon it in the melted state, a current of oxygen. The phosphorus burns under water, producing phosphoric acid, which is dissolved, and the red oxide, which is diffused as an insoluble red powder through the liquid ($3P+6O=PO_5+P_2O$). When it has subsided, and the vessel is cool, the water is poured off, and the red compound is digested in sulphide of carbon. This removes any uncombined phosphorus, and leaves the oxide. The oxide is an insoluble red solid, not inflammable in air unless mixed with phosphorus, when, if dry, it will take fire spontaneously. It burns on contact with nitric acid, and explodes when mixed with powdered chlorate of potassa. It is unchanged by dry air or oxygen; but in damp air, it is slowly oxidized. It is not luminous in the dark; it is not very inflammable when heated in air; but at a red heat, it is converted into phosphoric acid and phosphorus ($5P_2O=PO_5+P_9$). Like allotropic phosphorus, it is insoluble in sulphide of carbon, and in all liquids which dissolve phosphorus. It is neutral, and enters into no combinations.

Hypophosphorous Acid ($PO,2HO$, or $3HO$) is prepared as follows:—Upon one part of phosphide of barium pour four parts of water, and when the evolution of phosphuretted hydrogen gas has ceased, pour the whole upon a filter. To the filtered liquid add sulphuric acid, as long as any precipitate falls: separate the precipitate, which is sulphate of baryta, and the clear liquor now contains hypophosphorous acid in solution. When concentrated by evaporation, a sour viscid liquid is obtained, incapable of crystallization, and eagerly attractive of oxygen. The concentrated acid is of the consistency of syrup; it has not been obtained free from water, with two, or, according to some, with three equivalents of which, it is always combined.

In place of the phosphide of barium, bisulphide of barium and phosphorus may be employed. When these are boiled in water, sulphuretted hydrogen escapes, and a hypophosphite of baryta is formed ($BaS_2+P+2HO=2HS+BaO,PO$). When potassa, soda, or lime is boiled with phosphorus in water, phosphuretted hydrogen escapes, and a hypophosphite of the alkali is formed and dissolved. The salt may be obtained on careful evaporation, although there is a liability to explosion if it is carried to dryness.

When hydrated hypophosphorous acid is heated, it is decomposed with the evolution of phosphuretted hydrogen, and the production of phosphoric acid: $2PO+3HO=PH_3+PO_5$. It is a powerful deoxidizing agent. It reduces the salts of gold, silver, mercury, and copper, to the metallic state ($PO+4AgO=Ag_4+PO_5$). When boiled with sulphuric acid, it decomposes it; sulphurous acid is evolved, and sulphur is deposited. An acid solution of permanganate of potassa is deoxidized in the cold, and the color is discharged by this acid. In combination with bases it forms *hypophosphites;* they are soluble in water, and many of them in alcohol; they are decomposed by a red heat; they are mostly deliquescent, and uncrystallizable, but some are inflammable and even explosive when heated.

Phosphorous Acid (PO_3).—The volatile white substance which has been mentioned as one of the products of the combustion of phosphorus in rarefied air, consists chiefly of this acid in a dry state. By burning phosphorus in a tube with a limited access of dry air, and caution as to temperature—as, for instance, by placing a piece of phosphorus near one end of a tube two or three feet long, drawn out at the ends, inflaming it, and gently propelling dry air through the tube—this acid may be collected in the form of a white volatile powder. It has the odor of garlic, and when exposed to air, rapidly absorbs moisture as well as oxygen, and is converted into phosphoric acid. The solid acid may be volatilized by heat in carbonic acid or nitrogen, but when moderately heated in air, it takes fire and burns, producing phosphoric acid ($5PO_3=3PO_5+P_2$). The slow combustion of phosphorus in air at a low temperature is attended with the production of this acid (PO_3). If sticks of phosphorus be placed in glass tubes, open at both ends, and arranged round a glass funnel inserted in the neck of a bottle, the phosphorus will slowly disappear, as if by deliquescence, and the liquid collected in a bottle will be chiefly a solution of this acid, mixed with some phosphoric acid. It was formerly called *phosphatic* acid. When the hydrated acid is heated, or when its solution is evaporated to dryness, phosphuretted hydrogen is evolved, and it is converted into phosphoric acid ($4PO_3+3HO=PH_3+3PO_5$). If may be obtained by evaporation *in vacuo*, as a crystalline hydrate (PO_33HO). The solution in water is not corrosive, but powerfully acid. When heated with zinc or iron, phosphuretted hydrogen is evolved, and phosphates of the metals are formed. The solution absorbs oxygen when exposed to air, and phosphoric acid is produced. It is a powerfnl deoxidizing agent. It reduces at a boiling temperature the oxide of mercury, permanganate of potassa, and the salts of gold and silver. In reference to the salts of silver the following changes take place: $PO_3+2AgO,NO_5=2Ag+PO_5+NO_5$. It deoxidizes sulphuric acid, converting it to sulphurous acid, and this again is decomposed and sulphur is deposited. It also deoxidizes nitric and arsenic acids, converting the latter into arsenious acid. In these reactions it is changed into phosphoric acid. The solution of this acid does not precipitate albumen. Chlorine converts it into phosphoric acid ($PO_3+2Cl+2HO=PO_5+2HCl$).

Phosphites.—The phosphites contain, according to Graham, three atoms of base to one of acid, the hydrated acid being the tribasic phosphite of water. Others regard the acid as dibasic—one atom of water being retained in its combination with two atoms of a metallic oxide. The affinity of the phosphorous acid for bases is but feeble. All the phosphites include water, and when sufficiently heated, are resolved into hydrogen and phosphates, often with combustion. At common temperatures they do not absorb oxygen from the air, but they are easily convertible into phosphates by nitric acid, chlorine, and other oxidizers. They have the characters assigned to phosphorous acid.

PHOSPHORIC ACID (PO_5).—Anhydrous phosphoric acid can only be obtained by the direct combustion of phosphorus in an excess of dry oxygen; intense heat and light are evolved, and white deliquescent flocculi line the interior of the receiver. The acid may be produced by burning phosphorus under a tall receiver in atmospheric air, the air having been previously well dried by placing under the receiver a saucer containing sulphuric acid. The receiver should be placed in a glass dish, and should rest upon some thick pieces of plate-glass. A piece of phosphorus in a platinum or porcelain capsule, may be ignited and covered over with the receiver. The phosphorus burns at first furiously, but the combustion gradually subsides for want of oxygen, and may be renewed by gently lifting the receiver off the glass plates: thus the whole of the phosphorus may be gradually consumed, and it forms a quantity of dense vapor, which subsides in the form of white flakes like snow, some portions adhering to the sides of the glass. A convenient apparatus has been constructed for burning phosphorus in oxygen, so as to produce this acid in large quantity. The solid phosphoric acid obtained by this process, should be transferred as quickly as possible into a dry stopper-bottle, in which it may be pressed down: and the portions of acid which remain adhering to the receiver and dish, may be washed out, and they will yield a solution of the acid.

In the anhydrous state, phosphoric acid is an extremely deliquescent uncrystalline white powder, fusible into a vitreous substance, and volatile at a full red heat. It is inodorous, not acid in the dry state, and not corrosive. A small quantity of water poured upon the solid acid, dissolves it with a hissing noise, and great heat is evolved. A solution of the protohydrate of phosphoric acid is thus obtained. The liquid is sour to the taste, and powerfully acid in reaction. Anhydrous phosphoric acid is occasionally employed in chemistry for the purpose of dehydrating liquids by distillation. At high temperatures it is decomposed by charcoal, and by several of the metals. It combines with hydrate of lime to form a hard cement, which has been used for stopping teeth. The acid consists of:—

	Atoms.	Equiv.	Per cent.
Phosphorus	1	32	44·4
Oxygen	5	40	55·6
Phosphoric acid	1	72	100·0

Mr. Graham has shown that phosphoric acid occurs in three peculiar or isomeric conditions, which may be designated, 1. Metaphosphoric acid, or *a* phosphoric acid; aPO_5: 2. Pyrophosphoric acid, or *b* phosphoric acid; bPO_5: 3. Common phosphoric acid, or *c* phosphoric acid; cPO_5. The first combines with *one*, the second with *two*, and the third with *three* atoms of water or base. The acid is regarded, by Graham, as the same in all these modifications, which are supposed to depend upon the proportion of water or base with which it is in union: so that aPO_5 may become bPO_5 by the acquisition of a second atom of water or of base, and cPO_5 by a third; and inversely cPO_5 by losing an atom of base or of water, becomes bPO_5, and this by the further abstraction of base or basic water, passes into aPO_5, and aPO_5 losing its single equivalent of water or base reverts to PO_5. In accordance with this view, phosphoric acid intimately combined with one atom of water, only allows of the replacement, by substitution, of that atom of water by one atom of base: but if the original acid be similarly united with two or three atoms of water, these are then replaced by two or three atoms of base.

PO_5HO. *Protohydrate* or *Monobasic Phosphoric Acid; Metaphosphoric Acid.*—Aqueous solutions of any of the modifications of phosphoric acid, when evaporated and heated until they cease to lose water, yield the protohydrate, in the form of what has been termed *glacial phosphoric acid.* In this state it contains 11·2 per cent. of water. When phosphate of ammonia is heated to expel the alkaline base, this acid remains as a glassy-looking residue. The white anhydrous phosphoric acid procured by burning phosphorus in dry air or oxygen, when dissolved in water forms a solution of the protohydrate. It is characterized by producing a white precipitate in a solution of albumen; and in solutions of baryta, lime, and oxide of silver, it gives peculiar white precipitates like soft solids, without crystallization. These compounds contain one atom of base to one of acid.

$PO_5,2HO$. *Bihydrate or Bibasic Phosphoric Acid. Pyrophosphoric Acid.*—When a solution of pyrophosphate of soda (obtained by heating the phosphate to full redness) is precipitated by acetate of lead, and the insoluble salt of lead is washed and decomposed by sulphuretted hydrogen, an acid liquid is obtained, which must be left in a shallow basin until the sulphuretted hydrogen has escaped; it is then an aqueous solution of pyrophosphoric acid. It yields the pyrophosphate, when neutralized by carbonate of soda; gives a *white* precipitate with nitrate of silver; and forms salts, all of which have two atoms of base. The acid, before neutralization, does not precipitate solutions of nitrate of silver or of baryta, and it does not precipitate albumen. A diluted solution of this bihydrate of phosphoric acid, may be preserved without change; but when it is boiled for some time, it passes into the terhydrate. Graham and Peligot obtained this acid, not however quite free from terhydrate, by evaporating the solution of the terhydrate in a platinum flask, until its temperature attained 416°. It appeared as a soft glass. Peligot obtained it in opaque imperfect crystals resembling grape sugar.

$PO_5,3HO$. *Terhydrate or Tribasic Phosphoric Acid. Common Phosphoric Acid.*—The common phosphate of soda yields this acid, when a solution of the salt is precipitated by acetate of lead, and the phosphate of lead is decomposed by sulphuretted hydrogen; but it is generally procured by oxidizing phosphorus with nitric acid. The acid must be diluted with three parts of water in order to prevent too violent an action. Portions of phosphorus are introduced into a Florence flask and covered with the acid and water. The mixture is heated carefully, and as soon as red fumes appear, the heat is reduced, and the action is allowed to proceed ($3P+5NO_5=3PO_5+5NO_2$). When the acid is saturated, the liquid is evaporated, and the surplus nitric acid is expelled. It is finally concentrated to a syrupy state in a platinum dish. When dissolved in water, it forms the ordinary solution of phosphoric acid. A solution of the terhydrate may be prepared by boiling the monohydrate in diluted nitric acid. The conversion is rapid in a diluted solution and no bihydrate appears to be formed. The nitric acid in this case appears to act by catalysis (page 54).

In solution, it is very acid, but not corrosive, so that when heated on paper, the paper is not carbonized. It gives no precipitate with a solution of albumen or nitrate of baryta, or with a solution of nitrate of silver; but when united with a base, it gives with the latter salt, a yellow precipitate. It precipitates a solution of pure lime, but readily dissolves the precipitate, if the acid is added in excess. When heated to 400° it loses water, and becomes a mixture of proto and bihydrate; but it cannot be made anhydrous by heat, as it is volatilized in the state of protohydrate below a red heat. If kept below this temperature, it is entirely converted into protohydrate. Conversely, the proto and bihydrate, when kept for some time in solution in water, take one and two equivalents of water, and are ultimately converted into the terhydrate. This change is rapid when the aqueous solutions are weak and submitted to a boiling temperature, or when a little nitric acid is added. The acid liquid will no longer precipitate albumen, and when neutralized by an alkali, it will give a yellow precipitate with nitrate of silver. In general, water in combining with anhydrous acids in more than one equivalent, does not alter the properties of the acid. Thus there are three hydrates of sulphuric acid, but all have similar properties. In reference to phosphoric acid, the protohydrate, in its reactions on albumen and on a solution of nitrate of silver, is wholly different from the terhydrate; and the bihydrate differs from both.

The only impurity likely to be found in this acid, when made according to the method above described, is nitric acid. This may be detected by the usual tests (page 164). If any phosphorous acid is present, it may be detected by warming a portion with a solution of sulphurous acid. In this case, there will be a precipitation of sulphur; and if arsenic is present, it will be under similar circumstances thrown down as yellow sulphide of arsenic.

The constitution of the three hydrates of phosphoric acid may be thus represented:—

	Monobasic.			Bibasic.			Tribasic.		
	Atoms.	Weights.	Per cent.	Atoms.	Weights.	Per cent.	Atoms.	Weights.	Per cent.
Phosphoric acid	1	72	88.8	1	72	80	1	72	72·72
Water . .	1	9	11.2	2	18	20	3	27	27·28
	1	81	100·0	1	90	100	1	99	100·00

Phosphoric acid has less affinity for bases than the sulphuric, at ordinary temperatures, but as it is more fixed, it will expel the sulphuric acid from the sulphates at a high temperature.

Phosphates.—Each of the above hydrates of phosphoric acid forms a distinct class of salts, namely, *metaphosphates*, which are monobasic; *pyrophosphates*, which are bibasic; and *common phosphates*, which are tribasic; so that the proportion of fixed base with which the acid unites in the humid way, is dependent upon the proportion of water which the fixed base replaces. Thus, the metaphosphoric acid, or protohydrate, will only combine with one, and the pyrophosphoric or deutohydrate with two equivalents of soda; and if in either case a larger quantity of base be added, it remains uncombined; so also in regard to the terhydrate; if to one equivalent of it in solution, one equivalent of soda is added, one equivalent only of its water is displaced and two are retained: $3(HO)PO_5+NaO=NaO,2(HO)PO_5+HO$. On the addition of a second equivalent of soda, a second atom of basic water is displaced, the salt therefore still remaining characteristically tribasic; for in this case, $NaO,2(HO)PO_5+NaO$, becomes $2(NaO)HO,PO_5+HO$; and lastly, the addition of a third equivalent of soda displaces the remaining atom of water, and we have an anhydrous tribasic phosphate of soda: $2(NaO)HO,PO_5+NaO=3(NaO)PO_5+HO$. So also in regard to the insoluble phosphates formed by precipitation: the monobasic, or metaphosphate of soda, decomposes one equivalent of nitrate of silver, and a white monobasic phosphate of silver is thrown down: $NaO,PO_5+AgO,NO_5=AgO,PO_5+NaO,NO_5$. On the other hand, the bibasic salt, or pyrophosphate of soda, decomposes two equivalents of nitrate of silver to form a white bibasic phosphate of silver: $2(NaO)PO_5+2[AgO,NO_5]=2(AgO)PO_5+2[NaO,NO_5]$. And, lastly, one equivalent of the tribasic phosphate of soda decomposes three equivalents of nitrate of silver, forming one equivalent of the yellow or common phosphate of silver, and three of nitrate of soda. $3(NaO)PO_5+3[AgO,NO_5]=3(AgO)PO_5+3[NaO,NO_5]$.

The phosphates which are *soluble* are easily recognized by the addition of nitrate of silver. A yellow precipitate is thrown down. When acetate of lead is added to the solution, a white precipitate of phosphate of lead is formed, and this is not soluble in an excess of the phosphate. For neutral solutions the following plan may be adopted: Precipitate a solution of sulphate of magnesia, and add sufficient chloride of ammonium to redissolve the magnesian precipitate. This liquid added to the solution of a phosphate, even when much diluted, produces a white crystalline precipitate of phosphate of ammonia and magnesia, insoluble in ammonia and chloride of ammonium, but soluble in nitric and acetic acids. This precipitate when collected, dried, and calcined, is thus constituted: $2(MgO)PO_5$. In the absence of arsenic acid, it serves for the detection and estimation of phosphoric acid. In an acid solution of a phosphate the perchloride of iron is a useful reagent, not merely for the detection, but for the separation of phosphoric acid. Add to the diluted solution of a phosphate, acetate of soda and a few drops of a solution of perchloride of iron—a pale reddish-brown precipitate of phosphate of iron is thrown down. This precipitate is not soluble in acetic acid, but is dissolved by the hydrochloric and some other acids, hence, before the test is employed, it is advisable to nearly neutralize the solution. The precipitation is rendered more complete by boiling the liquid.

An *insoluble* phosphate (lime) should be first dissolved in diluted nitric acid. The acid solution gives a gelatinous or flocculent white precipitate of phosphate of lime, when the acid is neutralized by ammonia. It is insoluble in alkalies. If nitrate of silver is added to another portion of the acid liquid, and then a few drops of a weak solution of ammonia, the presence of phosphoric acid is indicated by the production of a yellow precipitate of phosphate of silver.

The whole of the phosphoric acid may be obtained from an insoluble phosphate, by dissolving it in diluted hydrochloric acid, nearly neutralizing the solution with ammonia, and then adding to it acetate of soda with a sufficient quantity of perchloride of iron to give a reddish color to the liquid. On boiling the liquid, the whole of the phosphoric acid is precipitated in combination with the oxide of iron. The *pyrophosphates* give white precipitates with solutions of nitrate of silver and acetate of lead. The lead-precipitate is dissolved by an excess of the solution of pyro-phosphate. When a pyrophosphate is added to a solution of albumen, and the liquid is acidulated with acetic acid, there is no precipitate.

The *metaphosphates* have the characters assigned to metaphosphoric acid (page 225). They precipitate the salts of baryta, lead, and silver. The white salt of silver is soluble in an excess of metaphosphate, in which respect it differs from the pyrophosphate.

PHOSPHORUS AND HYDROGEN. (*Phosphide of Hydrogen*).—Phosphorus forms three compounds with hydrogen, one gaseous, PH_3; one liquid, PH_2; and one solid, P_2H. The gaseous compound is that which is best known as a highly combustible, and in some cases spontaneously inflammable gas. This spontaneous inflammability is not, however, a property of the pure gas; but it depends on the admixture of the vapor of the liquid compound, which is generated at the same time. It is the spontaneous combustion of this vapor in air, which renders the phosphuretted hydrogen, associated with it, inflammable.

The pure phosphuretted hydrogen may be procured by acting on phosphide of calcium with strong hydrochloric acid. As thus procured, it is a colorless gas, having a fetid odor resembling that of onions or garlic. Some have compared it to the smell of putrid fish. It is soluble in water and alcohol. Water will take up about one-eighth of its volume. Although combustible at a comparatively low temperature, 212° (REGNAULT,) it does not burn spontaneously in air, unless it is mixed with the vapor of the second compound. In this case, it burns with a bright white light, producing solid phosphoric acid and water.

The mixed compound, containing the inflammable vapor, was for a long time considered to be the true phosphuretted hydrogen gas. It was discovered by Gengembre, in 1783, while the uninflammable variety was first made known by Davy, in 1812. The spontaneously inflammable gas is prepared by heating phosphorus in a very strong solution of potassa, a little ether being placed in the retort, to prevent an accident from explosion, when the gas is first produced. The gas does not burn in the vapor of ether. The changes which take place in its production may be thus represented: $3KO+4P+3HO=PH_3+3(KO,PO)$. It may be collected over water, and preserved in bottles in a dark place for more than a week, still retaining its property of spontaneous inflammability. If exposed to light, the vapor of the liquid PH_2 undergoes decomposition, and it is resolved into a solid phosphide of a yellowish color, and into the non-inflammable gas. This vapor may be separated from the gas, by passing it through a freezing mixture. It is also decomposed by hydrochloric acid, and in these cases, the gas loses the property of spontaneous inflammability. Deutoxide of nitrogen restores this property to phosphuretted hydrogen. (REGNAULT.)

When a bubble of this gas escapes into the air, it bursts and burns with the bright white light of phosphorus, producing an expanding wreath of white phosphoric acid vapor, which, as it slowly dissolves in the air, may be seen to be composed of numerous smaller wreaths, each rapidly revolving around a central axis, and at right angles to the expanding horizontal wreath. This motion appears to be dependent on the heated currents of air carrying the solid particles of phosphoric acid in their course. $PH_3,PH_2+O_{15}=2PO_5+5HO$. Bubbles passed into a jar of oxygen or of protoxide of nitrogen, burn with a brilliant light. In chlorine, they burn with a pale bluish light forming perchloride of phosphorus.

A quantity of this gas suddenly exposed, explodes with oxygen or air, and in the absence of sufficient oxygen for perfect combustion, red oxide of phosphorus is deposited in the vessel. The gas is frequently mixed with free hydrogen. This may be detected by a solution of sulphate of copper, which dissolves the phosphuretted hydrogen only. It is also absorbed by a solution of chloride of lime.

It has been long known that whether spontaneously inflammable or not, the gas had the same composition, a fact which is now intelligible, as the property is an accidental result of the admixture of another phosphide in vapor. Gay-Lussac and Thenard found that one volume of this gas, when decomposed by chlorine, gave three volumes of hydrochloric acid. This proved that each volume contained one and a half volumes of hydrogen, or two volumes of the compound contained three of hydrogen. The removal of the phosphorus from the gas by copper and potassium, establishes the accuracy of these volumetric proportions. The weight of phosphorus in each volume, is found by deducting one and a half times the specific gravity of hydrogen, from the ascertained specific gravity of the gas. This is as nearly as possible equal to one-fourth the specific gravity of phosphorus-vapor; hence one quarter of a volume of phosphorus-vapor is combined with one and a half volume of hydrogen, in each volume of phosphuretted hydrogen: or one half volume with three of hydrogen, in two volumes of the gas. Some chemists prefer doubling the volumes—thus making one volume of phosphorus-vapor to be associated with six volumes of hydrogen—the seven volumes being condensed into four. Its composition will, therefore, stand thus:—

	Atoms.	Equiv.	Per cent.	Vol.	Sp.Gr.
Phosphorus .	1	32	91·43	½	2·1777
Hydrogen . .	3	3	8·57	3	0·2073
	1	35	100·00	2	2·3850

The sum of the sp. gr. divided by 2 gives 1·1925. The specific gravity of the gas is commonly represented to be 1·1850 compared with air; and compared with hydrogen 17·5. It will be perceived that the gas has some analogy in its volumetric constitution to ammonia, but it has not the alkaline properties. It forms, however, solid crystalline compounds with the hydriodic and hydrobromic acids. The constitution of this gas shows that the atoms of elements are not necessarily represented by single volumes; and those of compounds by two volumes. On the former view, the atomic volume of phosphuretted hydrogen would be equal to four volumes of the compound; and on the latter view, the atom of phosphorus must necessarily be represented by half a volume (*see* page 66).

Phosphuretted hydrogen does not change the color of paper impregnated with a salt of lead; but it immediately decomposes solutions of silver and gold, the metals being reduced by it to the metallic state. The gas is absorbed and decomposed by these solutions. Thus the nitrate of silver forms a good test for the presence of this compound. When passed through a tube heated to redness, the gas is decomposed.

Liquid Phosphide of Hydrogen (PH_2).—This is procured by distilling fragments of phosphide of calcium with water only, and collecting the product in a receiver, kept cool by a freezing mixture. The phosphide thus procured is a most inflammable liquid. It takes fire in air, and burns with a brilliant light. It is colorless, highly refracting, and insoluble in water. It remains liquid at —4° ; is destroyed by a temperature of 86°, and when exposed to light is resolved into solid phosphide and non-inflammable phosphuretted hydrogen: $5PH_2=P_2H+3PH_3$. When its vapor is mixed with hydrogen it renders this gas spontaneously inflammable in air. It is decomposed by strong hydrochloric acid, and by oil of turpentine. When phosphide of calcium is put into water, gaseous phosphuretted hydrogen, with the vapor of liquid phosphide, escapes, and burns in the air with great brilliancy. The bubbles of gas are similar to those which are evolved, by boiling phosphorus in a strong solution of potassa.

Solid Phosphide of Hydrogen (P_2H).—This is analogous in constitution to the oxide, hydrogen being substituted for oxygen. It may be procured by exposing to light the liquid compound, or the spontaneously inflammable gas. It is of a yellow color, has an odor of phosphorus, but is not luminous in the dark. It is reddened by light. It is insoluble in water and alcohol. It is not inflamed in air under a temperature of 320°.

PHOSPHORUS AND NITROGEN.—A compound of these metalloids was announced by Rose under the formula N_2P. He procured it by saturating the pure terchloride of phosphorus at a low temperature with ammonia. The white substance thus obtained, when heated to redness out of contact of air, left a light white powder insoluble in water, alcohol, and ether. When excluded from air and moisture, it is fixed and infusible at a red heat, although its constituents are volatile. When heated in contact with air and moisture, it evolves white fumes of phosphoric acid, and becomes slowly oxidized without inflaming. Heated on platinum, it corrodes the metal, and converts it into a phosphide. According to Gerhardt, it contains hydrogen, and is in reality an amide of phosphorus, NH_2P, or *Phosphamide.*

PHOSPHORUS AND CHLORINE.—There are two compounds of these elements, a terchloride corresponding to phosphorous acid; and a pentachloride corresponding to phosphoric acid.

TERCHLORIDE OF PHOSPHORUS (PCl_3).—This compound, which is liquid, is procured by distilling a mixture of phosphorus and chloride of mercury; or, by passing the vapor of phosphorus over chloride of mercury heated in a glass tube, terminating in a cool receiver. This liquid dissolves phosphorus, and generally holds a little in solution, which gives to it a reddish color. When purified by slow distillation, it becomes limped and colorless; it requires it to be cautiously excluded from the action of the air. It has a suffocating odor. Its specific gravity is 1·45. Exposed to the air it is volatile, and exhales acid fumes: it does not change the color of *dry* vegetable blues, but becomes powerfully acid upon the least acquisition of moisture. Its vapor is combustible. It has a sp. gr. of 4·742; 3 vols. of chlorine are combined with $\frac{1}{2}$ vol. of phosphorus to form 2 vols. of the vapor. Chlorine converts it into pentachloride of phosphorus. It acts upon water with great energy, and produces phosphorus and hydrochloric acids, $PCl_3+3HO=PO_3+3HCl$.

PENTACHLORIDE OF PHOSPHORUS (PCl_5).—When dry phosphorus is submitted to the action of chlorine in excess, it burns with a pale yellow flame, and produces a white, flaky, volatile and deliquescent compound, which attaches itself to the interior of the vessel, and which is the *pentachloride of phosphorus*. It may be conveniently formed in an exhausted retort, containing phosphorus, to which chlorine is admitted until the phosphorus is saturated. It was formerly mistaken for phosphoric acid, but its easy volatility is alone a sufficient distinction, for it rises in vapor at 200°. It is fusible under pressure, and crystallizable in transparent prisms; it is a non-conductor of electricity; it reddens dry litmus-paper, in consequence, as Berzelius supposes, of its acquiring hydrogen and oxygen from the decomposition of the paper. It fumes in the air, and when brought into contact with water, a mutual decomposition immediately takes place, and phosphoric and hydrochloric acids result. $PCl_5+5HO=PO_5+5HCl$. It is combustible, and produces chlorine and phosphoric acid by its combustion. When passed through a red-hot porcelain tube with oxygen, phosphoric acid is produced, and chlorine is evolved; these facts show that oxygen, at a red heat, has a stronger attraction for phosphorus than chlorine. Potassium, heated in its vapor, burns with great brilliancy: with dry sulphuretted hydrogen it yields hydrochloric acid and chloro-sulphide of phosphorus: $PCl_5+2HS=PS_2Cl_3+2HCl$. Metallic oxides decompose it with the production of metallic chlorides and phosphates. The vapor has a sp. gr. of 3·66. It consists of one half vol. of phosphorus and 5 vols. of chlorine condensed into 4 vols. of the compound.

There is an oxychloride, PCl_3O_2, which requires no particular notice.

PHOSPHORUS AND BROMINE.—There are two bromides of phosphorus—a liquid and a solid—corresponding to the two chlorides (PBr_3, PBr_5). The elements combine on contact with explosive violence, hence great caution should be used in preparing these compounds.

PHOSPHORUS AND IODINE.—Iodine combines with phosphorus on contact, producing combustion when the mixture is exposed to air. There are two iodides, a biniodide, PI_2, and a teriodide, PI_3. They are both solid and crystalline; they may be procured by dissolving the constituents in their equivalent proportions in sulphide of carbon, and cooling the solutions.

PHOSPHORUS AND SULPHUR.—These elements combine, according to Pelouze and Fremy, to form five different compounds, four of them corresponding to the four oxygen-compounds of phosphorus—sulphur being substituted for oxygen. Besides these, there is the persulphide PS_{12}. to which there is no analogous oxygen compound. Sulphur and phosphorus may be combined by fusion in an atmosphere of carbonic acid, but great caution should be used, as with common phosphorus a violent explosion may occur. The phosphorus should be melted under water, and the sulphur gradually added in small fragments. Phosphorus will thus combine with a large quantity of sulphur without losing its liquid state. Sulphur or phosphorus may be obtained in crystals from this mixture on cooling, according to whether one or the other happens to be in excess. Amorphous phosphorus may be fused with sulphur under these circumstances, without giving rise to an explosion, although there is a violent action when fusion takes place. (KEKULÉ.)

CHAPTER XIX.

CARBON AND ITS COMPOUNDS WITH OXYGEN. CARBONIC OXIDE. CARBONIC ACID.

THE carbon group of metalloids comprises three bodies—carbon, boron, and silicon. Carbon is the great constituent of the organic, and silicon of the inorganic kingdom. Boron is not found among organic products, and is only sparingly diffused in the mineral kingdom. These bodies do not enter into combination with each other; but they have certain characters in common. They exist either in a crystalline or amorphous state; in the latter state, they assume the form of black or dark-colored solids, which may be heated in close vessels without change, but undergo combustion and oxidation when heated in air. Carbon entirely disappears as a gaseous acid, (carbonic acid), while boron and silicon are converted into white fusible solids (boracic and silicic acids). These three bodies cannot be made to assume the vaporous condition, although they readily combine with other metalloids to form gaseous compounds. As a summary of their characters, they are chiefly remarkable for being in the crystalline state intensely hard; and in the amorphous state, insoluble, and fixed at the highest temperatures. Carbon is infusible, but boron and silicon may be fused at a very high temperature.

CARBON (C=6).

History.—Carbon is found in various states which are considered to be allotropic modifications of the same elementary substance, but widely differing from each other in appearance and physical properties. In its purest form, it constitutes—1, diamond, which is crystallized carbon. In a less pure state, it is seen in—2, plumbago or graphite; 3, as anthracite; and 4, as coke, the carbon of coal. The state in which it is most commonly seen is—5, as *charcoal*, derived either from animal or vegetable matter.

All these varieties agree in the fact that when heated to a high temperature in oxygen or air, they undergo combustion and are converted into carbonic acid. The combustibility, however, varies greatly with the molecular condition of the carbon. Tinder, the carbon of linen or cotton, is easily ignitable, and when once ignited, combustion spreads readily throughout the mass; but a piece of wood charcoal or coke, if ignited, is soon extinguished on exposure to air. Animal charcoal, in consequence of its hardness, and the very large quantity of mineral matter associated with it, burns with difficulty. Plumbago and diamond, owing to their compact texture, require to be heated to a very high temperature in pure oxygen, before they will readily undergo combustion. The diamond finely powdered, may, however, be burnt by heating it on red-hot platinum; diamond dust heated with sulphuric acid and bichromate of potassa, is said to be completely converted into carbonic acid. (ROGERS.)

Carbon is essentially the element of the organic kingdom. All organic substances, or those which have been produced under the influence of life, contain it. It constitutes nearly half the weight of the dried animal or vegetable substance. In the vegetable kingdom, it forms the skeleton of the plant or tree—a fact which is made evident to us by the perfect preservation of form, when the substance has been heated out of contact with air. The detection of carbon in the residues of substances heated to redness in close vessels, is properly relied upon as the best evidence of the presence of organic matter. Carbon is, however, an important constituent of the mineral kingdom. Apart from its crystalline forms in diamond and plumbago, it is found as anthracite, bituminous coal, and lignite, in vast deposits in the earth. Limestone, marble, chalk, and coral, contain carbon (in a combined state as carbonic acid) in the proportion of about twelve per cent. of their weight; and in the atmosphere, carbonic acid (which contains twenty-seven per cent. by weight of carbon) is universally found. There is reason to believe that it is through this medium that carbon finds its way into the vegetable structure ; and that the oxygen associated with it, is restored to the atmosphere to be again converted by animals into carbonic acid. Carbon is also present, as carbonic acid, in rain, spring, and river-water.

DIAMOND (ἀδάμας, signifying hardness).—This substance has been found in India, Borneo, the Brazils, and Siberia. Diamonds have hitherto been met with in detached crystals, in alluvial soils, associated with rolled quartz-pebbles, sand, and a ferruginous clay. They are obtained by simply washing the soil; their great specific gravity facilitating their separation from the light sand and clay. Diamonds are now chiefly procured from the district of Serra do Frio, in the province of Minas Geraes, in the Brazils.

The primitive form of the diamond is a regular octahedron, each triangular facet of which is sometimes replaced by six secondary triangles, bounded by curved lines; so that the crystal becomes spheroidal, and presents forty-eight facets. Diamonds, with twelve and twenty-four facets, are not uncommon. The diamond has been found of various colors; those which are colorless are most esteemed ; then those of a decided red, blue, yellow, pink, or green tint. Those which are brown are least valuable. Three-fourths of the stones found, are tinged with some color, mostly pale yellow or yellow brown.

The fracture of the diamond is foliated, its laminæ being parallel to the sides of a regular octahedron. Although the hardest of bodies, it is brittle, and is easily broken when struck in its planes of cleavage, which are four, corresponding to the octahedral sides. Its specific gravity varies from 3·5 to 3·6: it is most commonly 3·52. Its specific heat is 0·1192. It is a non-conductor of electricity, and acquires positive electricity by friction. It conducts heat so much better than glass, that this property is sometimes employed as a test, to distinguish the diamond from substances which resemble it. It exerts a highly refractive power on light: compared with glass or rock-crystal it is 2·47 to 1·6. When exposed for some time to strong sunshine, it becomes, by insolation, luminous in the dark. The strongest alkalies and acids, including the fluoric acid, whether singly or in mixture, have no effect upon it. The fluoric acid, however, dissolves and destroys artificial or *paste* diamonds. With the exception of oxygen, the metalloids, including fluorine, have no action upon it; and oxygen will only combine with it at a very high temperature. Its combustibility was first proved in 1694. It requires a most intense heat to effect this. It may be burnt in a vessel of pure oxygen by concentrating upon it the solar rays, or by heating it in the flame of the oxy-hydrogen blowpipe, and then introducing it into a bell-jar of pure oxygen. In the atmosphere, however heated, it will cease to burn so soon as the current of air is withdrawn. It has been clearly proved that carbonic acid is the sole product of this combustion, and that equal weights of pure carbon and diamond yield the same quantity. The diamond, like other kinds of carbon, deflagrates with melted nitrate of potassa, and produces carbonate of potassa. During its combustion in oxygen, it evolves, without flame, a bright light, which is even visible in sunshine; and it occasionally leaves a slight incombustible residue. Some diamonds have been entirely consumed in oxygen; others have left a residue of silica and oxide of iron, varying from 0·15 to 0·2 per cent. of their weight—a quantity so small, that it may be regarded as an accidental impurity. The black, or carbonic diamond (*carbonado*), found at Bahia, in Brazil, in 1843, when burnt, leaves a larger residue. Three samples left respectively residues weighing 0·24, 0·27, and 2·03 per cent. of their weight. (DUMAS.) The sp. gr. of this variety of diamond, which is chiefly used for making polishing powder, is from 3·1 to 3·43. It is the diamond in an amorphous state, quite opaque, and varying in color from iron-gray to reddish-black. In two years, four thousand ounces were extracted in Bahia.

When a diamond is heated on charcoal in the arc of fire from a powerful battery, it softens, cracks, increases in size, becomes black, and assumes the appearance of coke. Its sp. gr. is reduced from 3·3 to 2·6. In this state it is a conductor of electricity: it scratches glass, but is so brittle that it can be broken between the fingers. The effect of intense heat in thus destroying the transparency and completely changing the molecular condition of the diamond, appears to show that this substance, as it is found in nature, has not been exposed to a high temperature in its production. All attempts to fuse or crystallize carbon, or to form diamonds artificially, have hitherto failed. Some suppose that the carbon of diamond is of organic origin; but all that we can surmise is, that it has been crystallized from some unknown solvent. Olefiant gas and the sulphide of carbon are colorless compounds of this element. The sulphide, which is a liquid compound containing one-sixth of its weight of carbon, has, like the diamond, high refracting powers. If the sulphur could be slowly withdrawn from it by any artificial process, the carbon might be separated in a crystalline state. This liquid dissolves sulphur and yields it in octohedral crystals like those found in nature. When carbon is separated from olefiant gas, ether, oil of turpentine, and other transparent gases and liquids, it always assumes the black, or amorphous condition. The diamond, it is to be observed, is not always found crystallized in a regular form. Sometimes the substance has presented only a crystalline structure, at others, as in the black diamond, it has been found amorphous, having the appearance of intensely hard black charcoal.

The art of cutting and polishing diamonds, though probably of remote antiquity in Asia, was first introduced into Europe in 1456, by Louis van Berquen, of Bruges, who accidentally discovered that, by rubbing two diamonds together, a new surface or facet was produced. The forms which are given to the polished diamond are the brilliant and the rose. The brilliant form, which has from 56 to 64 facets, was first introduced by Cardinal Mazarin, in 1650. It is especially calculated to bring out the lustre and refractive powers of the gem. Thus a well-cut brilliant, held in a beam of light, reflects nearly the whole of the light which falls upon it, throwing it out and refracting it in colored rays through the facets in front. With the exception of one small point of light through the *collet*, the brilliant forms an opaque shadow on a screen.

The diamond appears to be unchangeable, and the most indestructible of substances. The *Koh-i-Noor*, said to have been discovered in 1550, and now among the British crown jewels, had undergone no apparent alteration in brilliancy or polish after the lapse of three hundred years. The weight and value of diamonds is usually estimated in *carats*, of which 150 are about equal to one ounce troy, or 480 grains; *i. e.*, each carat is equivalent to 3·2 grains. The Koh-i-Noor, when first discovered, is stated to have weighed 900 carats. It lost by the first cutting 279 carats, and it has been considerably reduced by its having been recently cut into the shape of a brilliant. Its weight is now said to be 102 carats. The Russian diamond, the *Koh-i-Toor*, weighs 193 carats, but in consequence of its irregular shape, its value is small in proportion to its weight. Probably the finest diamond in the world, for its water, shape, and size, is the Pitt diamond, now among the crown jewels of France. It was discovered in 1702, and was purchased in the rough state by Mr. Pitt, governor of Bencoolen. In 1717, it was sold to the Regent Duke of Orleans, during the minority of Louis XV., for the sum of 135,000*l.* It was cut into the form of a perfect brilliant, and proved to be of the finest water, without color or flaw. It weighed, before cutting, 410 carats, and after cutting, 136. The chips and dust obtained from it, were valued at 8000*l.* In 1791 a commission of jewellers assigned its value at 480,000*l.* It is remarkable that these three large diamonds were found in the same district of Central India. The cutting and polishing of diamonds is chiefly carried on at Amsterdam.

Apart from its use in ornamental jewellery, the diamond is employed in the arts. Owing to its hardness, it is found a useful substance for the pivot-holes of watches. It has been employed for microscopic lenses, and it is extensively used for cutting glass. The edge of one of the small curvilinear crystals is selected for this purpose, as the edges of the crystals formed by flat planes, only scratch the surface, without producing that peculiar fissure by which the glass can be smoothly cut.

The diamond possesses none of the ordinary properties of carbon, as they are known in charcoal. This, no doubt, depends on the different molecular states of the two bodies.

PLUMBAGO. GRAPHITE. BLACK LEAD.—This substance is well known in the manufacture of pencils, for which purpose it is almost exclusively obtained from the mine of Borrowdale, at the west end of Derwent Lake, in Cumberland, where it was first wrought during the reign of Elizabeth. In a less pure state, it is not an uncommon mineral, occurring in detached masses, generally in primitive rocks. It is thus found in Germany, France, India, Ceylon, and North and South America. It is of an iron-gray color, metallic lustre, and soft and greasy to the touch, producing a leaden mark on paper. Its specific gravity varies from 1·9 to 2·5; it occasionally occurs crystallized in hexagonal plates; it conducts electricity, and, for this purpose, is much used in the electrotype process. It is infusible, very difficult of combustion, and when mixed with fire-clay, is a useful ingredient in the manufacture of crucibles and melting-pots intended to withstand high temperatures. It undergoes no change in air, and is used to cover articles of iron to prevent them from rusting. When it is burned in a stream of oxygen gas, it leaves a small quantity of yellow ash, composed chiefly of oxide of iron, with silica and titanic acid, but varying in quantity in different specimens. In good plumbago, the carbon amounts to 96 per cent. Some specimens from Brazil leave scarcely any residue when burnt. The oxide of iron is an incidental ingredient, and is not in chemical combination with carbon. It exists in no definite proportion. The late Mr. Brockedon found that the dust of plumbago might be forced, under great pressure (like spongy platinum), into a coherent mass, which might be cut and applied to the same uses as the pure native substance.

Cast-iron, after corrosion, as a result of long immersion in sea-water, acquires the softness, greasiness, and some other physical characters of plumbago. The cannon-balls and cast-iron guns of the *Royal George*, sunk at Spithead, presented this condition after many years' submersion in sea-water. A mass of cast-iron, which had been immersed some years in a brewer's vat, had a loose and spongy structure, and was so soft that it could be cut with a knife. It appears from analysis that, in this transformation, the greater portion of the iron is removed, and the carbon largely predominates. The durability of cast-iron piers, sunk in sea-water, may be affected by this change.

Mr. Brodie has found that plumbago is remarkably altered in its chemical and physical properties, when it is heated with sulphuric acid and chlorate of potassa.

CARBON OF COAL.—The principal constituent of coal is carbon, associated with variable proportions of oxygen and hydrogen, as well as with small quantities of sulphur and nitrogen. The British caking or bituminous coals, including those of Northumberland, Nottinghamshire, and South Wales, have a sp. gr. of about 1·2; and according to Dr. Percy, they contain from 77 to 83·44 per cent. of carbon. The British non-caking coals contain from 72 to 80 per cent. of carbon; while cannel coals contain 78 to 84 per cent. (PERCY, *Metallurgy*, p. 99.) All kinds of coal yield an ash consisting of silica, oxide of iron, and lime. In good coal this varies from one to three per cent. of its weight. In the bituminous schists, such as the Torbane mineral, miscalled coal, the ash amounts to 25 per cent. of the weight of the substance.

The chief characters of good coal are that it is a black, brittle, combustible substance, containing a large amount of carbon, of which it will yield about half of its weight, under the form of coke, when it is heated out of contact of air. The amount of mineral ash which is left, after perfect combustion, is small, and does not interfere with the use of the substance for heating purposes.

In *Lignite*, or wood coal, which forms one end of the coal series, the shape and structure of the wood are preserved. In *Bituminous*, or pit-coal, the vegetable structure is in great part lost, probably as a result of heat and compression. *Anthracite*, or stone-coal, called also mineral charcoal, contains a larger proportion of carbon than the other varieties. It is very heavy, having a specific gravity of 1·4, to 1·8, and has no resemblance whatever to wood. It is well known as the *culm* of Wales, and the *Kilkenny coal* of Ireland. It has a slight metallic lustre, is very difficult of combustion, so that it will burn only in a strong current of air; and when ignited, it is consumed without flame, smell, or smoke. We have found good Kilkenny anthracite, to leave only 4.4 per cent. of a reddish-brown ash, consisting chiefly of oxide of iron and silica, so that this coal might be considered as mineral carbon in a state nearly pure. It constitutes the other extreme of the coal series.

COKE.—This is the carbonaceous residue of the distillation of pit-coal. It is manufactured on a large scale in ovens constructed for the purpose. The bituminous coal of Northumberland yields 66 per cent.; and that of Nottinghamshire, 63 per cent. of coke. Non-caking and cannel coals yield rather less. Coke has a sp. gr. of 1·6 to 2, but in equal bulks it is about one-half the weight of coal. It has a porous texture, and sometimes a metallic lustre. This is owing to the glazing or fusion of ashes upon the surface. It is difficult of combustion except in large masses, and under a rapid current of air. Small pieces, when removed from the fire red-hot, are soon extinguished. It contains sulphur, and yields, by combustion, sulphurous acid. If quenched with water while red-hot, sulphuretted hydrogen is produced by the decomposition of the water. It exceeds all fuels in the amount of heat which it evolves by combustion. Next to hydrogen, there is no body which consumes so large an amount of oxygen as carbon; but coke gives a more powerful and steady heat than wood-charcoal, hence it is largely employed as a fuel in furnaces. It will evaporate 74 times its weight of water. The harder the coke, the greater is its value as fuel. Dry coke does not absorb aqueous vapor like charcoal. It will not take up more than from 1 to 2½ per cent. in a humid atmosphere; but perfectly dry coke, placed in water, will absorb this liquid to the extent of half of its weight. 1000 parts of dry coke, according to Berthier, consists of carbon, 858; ashes, 115; volatile matters, ·027. Good coke should not yield more than 4 or 5 per cent. of ash. Certain hard kinds will yield from 10 to 15 per cent. of their weight.

CHARCOAL.—*Preparation.*—Charcoal may be obtained either from vegetable or animal substances. In order to procure it, it is necessary that the organic matter should be heated to a high temperature out of contact of air. If an ordinary splint of wood be burnt in air, the carbon is entirely consumed, and a white alkaline ash remains. If a similar splint ignited, is gradually lowered into a narrow test-tube, allowing only a slow combustion to go on at the mouth of the tube, a skeleton of the wood in charcoal will be obtained. Introduce between two layers of mica a slip of paper, and place a similar slip on the outside of the mica. When heat is applied beneath, the piece of paper which is protected from air, will be converted into charcoal, while that which is exposed will be consumed, leaving only a slight ash. If a sheet of paper, or a portion of lace, impregnated with a solution of phosphate of ammonia is dried and burnt in air, the carbon of the vegetable matter is obtained, retaining its perfect form (*see* page 220). Charcoal may be prepared for chemical purposes by heating to redness, in a crucible, pieces of box-wood, covered with sand, and keeping them in that state for about an hour, or until all volatile matters are expelled. They are thus converted into a black brittle porous substance, which appears to be essentially the same, from whatever kind of wood it has been procured. The stick of charcoal, when broken, should be equally black throughout. Sugar and certain other substances, which neither contain nitrogen nor leave any residue after combustion, when intensely heated in closed vessels, yield a pure charcoal; it always retains, however, traces of oxygen and hydrogen; thus, Erdmann and Marchand found in the carbon of sugar obtained at a white heat, 3·1 per cent. of oxygen, and 0·6 of hydrogen, and even after it had been subjected for three hours to the highest temperature of a blast-furnace, it retained 0·5 per cent. oxygen, and 0·2 hydrogen. In passing the vapors of certain hydrocarbons, and of oils, alcohol, and ether, through white-hot porcelain tubes, pure carbon is deposited. A variety of pure carbon is occasionally found in coal-gas retorts, and in the tubes connected with them, resulting from the decomposition of the first products of the distillation of coal. It has a gray color, and often exhibits a laminated texture; its streak is black, and it breaks with an earthy fracture: its specific gravity is about 1·8. It sometimes happens that the gas escapes through a crack in the retort, in which case a peculiar carbonaceous deposit is forming upon the surrounding brickwork, of a stalactitic character, an iron-gray color, and considerable lustre; it does not easily burn, nor does it soil the fingers. Some specimens, from their appearance, might be considered to be metallic: its specific gravity is about 1·75.

Common charcoal, employed as fuel, is usually made of oak, chestnut, elm, beech, or ash-wood, the resinous woods being seldom used. Young wood affords a better charcoal than large timber, which is also too valuable to be thus employed. The billets are formed into a conical pile, which, being covered with earth or clay, is suffered to burn with a limited access of atmospheric air, by which its complete combustion, or reduction to ashes, is prevented. Another, and a more perfect mode of preparing charcoal, consists in submitting the wood to a red heat in a kind of distillatory apparatus, consisting of cast-iron cylinders, from which issue one or more tubes for the escape of gaseous matters and vapors. This kind of charcoal is preferred for the manufacture of gunpowder. A third method of charring wood consists in exposing it to the action of highly heated steam, by which, according to Violette (*Ann. Ch. et Ph.*, 3me Sér., xxiii. 475), different modifications of charcoal may be obtained, especially adapted for the manufacture of gunpowder. In another memoir upon the same subject (*Ibid.* xxxii. 346), M. Violette arrives at the following conclusions: 1. That the quantity of charcoal obtained from wood decreases in proportion as the temperature increases. At 482° the average product of charcoal is 50 per cent.; at 572°, 33 per cent.; at 752°, about 20 per cent.; and at the temperature of fusing platinum about 15 per cent. 2. The quantity of charcoal varies with the duration of the process of carbonization, and is greatest when the process is slowly carried on. 3. The normal carbon of the wood is divided during carbonization into two parts, one of which remains in the charcoal, and the other escapes with the volatile products. This division varies with the temperature of carbonization; thus, at 482° the carbon remaining in the charcoal is double that which escapes: between 572° and 662° the two portions are equal, and at a high temperature the quantity which escapes is double that which remains. 4. The charcoal retains a quantity of carbon proportionate to the temperature of carbonization; at 482° it includes 65 per cent. of carbon; at 572°, 73 per cent.; at 752° 80 per cent.; and carbonized at a higher temperature it contains 96 per cent. of carbon, but at no temperature is the product, carbon, in a state of purity. 5. Charcoal, however prepared, always retains gaseous matter, varying with the temperature of its preparation; when made at 482° it amounts to half the weight of the charcoal; at 572° to one-third; at 662° to one-fourth; at 752° to one-twentieth; and at the highest temperatures to about one one-hundredth. The preceding facts show the great influence of temperature, and of the duration of the carbonizing process, upon the produce of charcoal from the same wood. 6. When wood is carbonized in perfectly close vessels, the resulting charcoal retains nearly the whole amount of carbon; when thus charred, at between 300° and 660°, the percentage of carbon in the charcoal is about 80, which is thrice that contained in charcoal prepared in the usual way. 7. In ordinary carbonization, the so-called *brown charcoal* (*Charbon roux*) is not obtained under 518°, and the quantity amounts to about 40 per cent.; but in a perfectly air-tight vessel the quantity obtained is 90 per cent., and the temperature at which it is formed is 356°. 8. Wood, inclosed in a perfectly air-tight vessel, and subjected to a temperature of from 572° to 752°, undergoes a species of fusion; it agglutinates and adheres to the vessel; on cooling, it has lost all organic texture, and is a black, shining, porous, fused mass, exactly resembling pit-coal which has undergone semi-fusion. This seems to explain the formation of coal. 9. Charcoal made in perfectly close vessels contains ten times more ash than common charcoal, so that the volatile matters which escape during the ordinary process of carbonization or distillation, carry with them, either blended or combined, a large proportion of the mineral substances which constitute the ashes. 10. Charcoal, prepared in the ordinary way, varies much in quality and composition, in consequence of the variation in temperature and time consumed in the process of charring. The position of the pieces of wood in the cylinders, namely, whether central or external, in reference to their contents, affects its quality, a matter of much inconvenience in the manufacture of gunpowder. Charcoal obtained by the action of highly heated steam, is of a more uniform character than that which is produced as a result of partial combustion in a stack.

The quantity and quality of charcoal obtained from different kinds of wood are liable to much variation, according to the temperature and mode of charring. The following table shows the produce of charcoal from 1000 parts of several varieties of dense and light woods after exposure to a very high temperature out of contact of air.

Ebony	305
Botany Bay-wood	281
Brazil-wood	260
Eveoas-wood	225
King-wood	220
Tulip-wood	208
Satin-wood	207
Box	202
Fir	181
Lignum-vitæ	175
Oak	174
Mahogany	157
Beech	150

The ashes left by charcoal after complete combustion, vary in quantity with the kind of wood from which it has been procured. Ordinary charcoal used as fuel leaves, on an average, 2 per cent. of ashes, consisting chiefly of carbonate of potash, silica, lime, and oxide of iron. The results of experiments on this subject have shown that 1000 parts of charcoal from the wood of the lime-tree yields of ashes 50 parts; the charcoal of the oak, 25; of the birch, 10; of the fir-tree, 8; of the hornbeam, 26; and of the beech, 30 parts. There is a great loss of carbon in the ordinary methods of preparing charcoal. Thus, assuming that green wood contains 38·5 per cent. of this element, the most perfect processes of carbonization do not give a product greater than 27 or 28 per cent., and the common plan adopted in forests is so wasteful that not more than 17 to 18 per cent. are obtained. The loss is occasioned partly by the production of carburetted hydrogen, and, as a result of combustion, carbonic acid; and partly by the formation of tar and acetic acid.

Properties.—Wood-charcoal is a black, amorphous, insoluble, inodorous, insipid, opaque, and brittle substance. It preserves the form of the wood, is very porous, containing much air, and has a ringing metallic sound. Its pores may be injected and made visible by cooling it when red-hot under mercury. Unlike the diamond, it is a good conductor of electricity, but a bad conductor of heat, especially when in the state of powder. It is unchanged by the combined action of air and moisture at common temperatures. It is easily combustible in oxgen gas. Its specific heat, as estimated by Regnault, is 0·2411. When pure it is perfectly infusible at all known temperatures; in the cases in which it was supposed to have been fused, the fusion was owing to the presence of silicates in the ashes. Under common circumstances of ignition, it does not appear to volatilize, but it is not improbable that in the process of steel-making the penetration of iron by carbon, may be partly due to its volatility; and in the voltaic ignition of charcoal-points, carbon passes from the positive to the negative side in the arc of flame: so that a concavity is formed upon the surface, when the + electricity emanates, and a deposit of carbon upon the opposite pole. The intense white light produced in the passage of the electric fluid, is owing to the incandescence of the minute particles of carbon transferred from one pole to the other. In air, there is combustion, but when the experiment is performed *in vacuo*, the light is just as brilliant, and in this case, it must be exclusively due to incandescence. The specific gravity of charcoal is about 1·7. It readily floats on water, owing to the large quantity of air within its pores. If a piece of charcoal, after having been heated to full redness for some time, is suddenly cooled under water, it will acquire its proper density and sink. Ordinary charcoal, sunk in a jar of water by attaching to it sheet-lead, will be found to yield, *in vacuo*, a large quantity of air, chiefly from the broken ends. Pieces of charcoal placed in a jar full of water, inverted in a basin, will give out a large portion of the air which they contain. When strongly heated out of contact of air, it becomes harder and closer in texture, and is rendered a better conductor of heat and electricity. When heated in a current of air, it is consumed, leaving a white or reddish-white ash (*see* p. 239). Water, alcohol, ether, hydrochloric acid, and solutions of chlorine and hydrofluoric acid, have no action upon it. It is slightly dissolved by strong sulphuric acid, giving to it a brownish color; and by the aid of heat it decomposes nitric acid. It is this indifference to chemical agents, which renders charred wood, such as piles sunk in the earth, indestructible. Some of these have been found entire after the lapse of many centuries.

Newly-made charcoal has the property of *absorbing* and fixing *gases* and vapors, including aqueous vapor. We have found that box-wood charcoal increased in weight 14 per cent. within 24 hours. The average increase from this absorption is from 10 to 12 per cent. The researches of Saussure have proved that different gases are absorbed by charcoal in different proportions, and that the absorption attains its maximum in 24 hours. Damp charcoal does not absorb gases so readily as that which is dry. If charcoal is heated red-hot, cooled under mercury, and then introduced into a graduated tube containing a gas, the results may be easily observed and compared. Assuming that one cubic inch of charcoal is employed in the experiment, then, according to Saussure, the number of cubic inches of each gas absorbed will be represented by the figures in the following table:—

Ammonia	90	Olefiant gas	35·
Hydrochloric acid	85	Carbonic oxide	9·42
Sulphurous acid	65	Oxygen	9·25
Sulphuretted hydrogen	55	Nitrogen	7·5
Protoxide of nitrogen	40	Light carburetted hydrogen	5.
Carbonic acid	35	Hydrogen	1·75

It has been observed that the temperature of the charcoal rises as the gas is condensed within its pores. When charcoal, already saturated with any one gas, is put into another, it gives out a portion of the gas already absorbed, and takes up a portion of the new gas. It would also appear that this absorptive quality partly depends upon the mechanical texture of the charcoal, and consequently varies in the charcoals of different woods. According to Vogel, when recently-ignited charcoal, which has been cooled under mercury, is put into a jar of atmospheric air, it absorbs the oxygen of the air to a greater extent than the nitrogen. A piece of well-burned charcoal, cooled under sand, and then introduced into a mixture of oxygen and sulphuretted hydrogen gases, rapidly absorbed them: it then became ignited, and caused a violent explosion which shattered the bell-jar. In this experiment, which nearly led to a serious accident, a yellow vapor appeared to issue from the pores of the charcoal, just before the explosion took place. This was owing to the separation of sulphur. It is probable that the sulphuretted hydrogen employed was mixed with some free hydrogen. Thenard observed, that when fresh made and dry charcoal was saturated with sulphuretted hydrogen, and introduced into oxygen, the gases combined, with explosion, and water and sulphurous acid were produced. When the oxygen was mixed with nitrogen, the effect took place more slowly, and the hydrogen alone was consumed; there was at the same time a deposit of sulphur.

This property of charcoal is referred to catalysis (p. 54). It resembles the action of spongy platinum on certain mixtures of gases: but there is this difference between the two substances: Platinum has not the absorbent powers on gases which is manifested by charcoal, but it has a greater combining power. If coarsely powdered wood-charcoal is boiled in a solution of chloride of platinum, until it is thoroughly impregnated with the liquid, and is then heated to redness in a covered crucible, it will retain within its pores a residue of platinum: this substance is remarkable for its powers of absorption and combination.

To this property may be ascribed the power which charcoal possesses of absorbing and removing foul effluvia (*see* p. 212). A small quantity of powdered charcoal shaken in a jar of air containimg sulphuretted hydrogen gas, soon removes the smell. If water, containing sulphuretted hydrogen, is filtered through charcoal, it is speedily deodorized. The gas is first absorbed, and by a catalytic action the oxygen of the air unites to the hydrogen, while sulphur is deposited. The charring of the interior of a cask, intended to hold water for use at sea, has a similar influence on foul water put into it. Sulphuretted hydrogen is so completely removed, that the usual tests for the gas will fail to indicate its presence. Pans of powdered charcoal placed about a room in which there are foul effluvia, are thus efficacious in removing them. Putrescent animal matter is deprived of its offensiveness by covering it with powdered charcoal. If the charcoal should lose its power by long use, it may be easily restored by again heating it.

Experiments on a large scale have been performed by Dr. Letheby and Mr. Haywood, in order to determine how far charcoal could be practically employed for destroying the effluvia of public sewers. Well-dried charcoal, broken to the size of a filbert, was placed in trays in the current of air proceeding from a sewer—it thus acted as an air-filter. The result was most satisfactory; the foul effluvia were arrested and destroyed, and the charcoal, after from nine to twenty months' use, when treated with water, yielded an abundance of alkaline nitrate, a fact which proved that it had caused the oxidation of nitrogen in ammonia and other nitrogenous compounds. The absorbing and oxidizing powers of charcoal were greatly diminished when it was saturated with water, hence, owing to the absorption of moisture, the sieves required changing once in three months. If the charcoal is kept dry, there appears to be no limit to the oxidizing action of this substance. There can be no doubt from these experiments, that, by a proper use of powdered charcoal, the noxious effluvia of drains and sewers—the vehicles of typhoid fever—may be prevented from entering our dwellings. (*Report to Commissioners of Sewers*, Feb. 1862.)

But charcoal has not only the power of removing smells: it will also remove *colors*, and even, in some cases, the taste of liquids, where this depends on the presence of certain organic substances. Introduce into four bottles containing powdered charcoal, solutions of diluted sulphate of indigo, of cochineal, of the blue iodide of starch, and of the red permanganate of potassa. Agitate these liquids for a short time with the charcoal, and on filtration, it will be found that the colors are entirely removed. Port-wine may be rendered tawny or light colored by a similar process, thus giving to it the appearance of age. Impure solutions of sugar and of nitre, lose their colors by filtration through beds of charcoal—animal charcoal being preferred for this purpose. Other impurities which interfere with the crystallization of these substances are also removed. The crystallizable vegetable acids and alkaloids are thus brought to a high state of purity, but not always without loss. Mr. Warington observed that the sulphate of quinia was removed from its solution by charcoal, and that the bitterness of the hop may be entirely removed from ale by this substance, in the attempt to make dark-colored ale pale. Strychnia is so completely removed under these circumstances, that Mr. Graham has recommended it as the basis of a process for the detection of strychnia in liquids containing organic matter. As a medium of filtration, therefore, charcoal is eminently qualified to purify water. It removes color, taste, and smell. Charcoal obtained by the distillation of *peat*, or of *spent oak-bark*, used in *tanning*, possesses these properties in an eminent degree.

Charcoal has a great *deoxodizing* power, even at low temperatures. Portions of fresh-burnt box-wood charcoal, free from ashes, introduced into nearly neutral and very diluted solutions of gold, platinum, palladium, silver, and copper, separate the respective metals, which are deposited on the charcoal in thin films. The deposit of copper, if allowed to remain in the liquid, soon disappears. At a red heat, charcoal deoxidizes many fixed and volatile metallic oxides (arsenious acid), reducing them to the metallic state. It is in fact, the great reducing agent of metallurgists. At a white heat, owing to its fixedness, it deoxidizes even potassa, soda, and phosphoric acid, setting free in vapor, potassium, sodium, and phosphorus. It also decomposes water, producing carbonic oxide and hydrogen (water-gas). When the vapor of water is passed slowly over charcoal heated to full redness in a porcelain tube, or when an incandescent piece of charcoal is plunged under a jar in a water-bath, these gases are evolved, and may be collected : ($HO+C=H+CO$). But carburetted hydrogen and carbonic acid are also products of this decomposition. Bunsen found that in 100 parts of this *water-gas*, there were 56·03 hydrogen ; 29·15 carbonic oxide ; 14·65 carbonic acid ; and 0·17 of carburetted hydrogen.

Charcoal produces in the cold a violent explosion with perchloric acid: at a red heat, it deoxidizes the chlorates, perchlorates, and nitrates with deflagration, producing carbonates with the respective alkaline bases. At a full red heat it converts most of the sulphates to sulphides. It has no action on the haloid salts—namely, the chlorides, bromides, iodides, and fluorides, and it does not decompose at a high temperature silica and alumina. Its combinations with metals are called *Carbides*, or carburets. There is only one of these well known—namely, its compound with iron as cast-iron. Carbon is found as an impurity in aluminum, and in some other metals. Among the metalloids, it enters into *direct* union only with oxygen and sulphur, and even in reference to these bodies a very high temperature is required to bring about chemical combination.

Equivalent.—Tests.—The equivalent or atomic weight of carbon is fixed, by most chemists of repute, at 6. As it is unknown in the vaporous condition, its volume is of course hypothetical. For convenience, it is assumed to be the same as that of hydrogen, and is therefore taken as one or two volumes, according to the assumed volume-equivalent of that element. When *carbon*, as charcoal, is in a free state, it may be identified by its color, insolubility in all menstrua, its fixedness in close vessels, and its combustion and entire conversion to gaseous matter when heated in air. It may be also known when existing in any state, by its combustion, as a result of deflagration in melted nitre or chlorate of potassa, and by the production of carbonate of potassa. Carbon may, however, exist in such a form, in organic compounds, that with the exception of deflagration, these tests are no longer applicable for its detection. The substance suspected to contain it, should be well dried and mixed with four parts of dried black oxide of copper, or dry chromate of lead. The mixture inclosed in a small reduction-tube, bent at an angle, should be then gradually heated to redness—the mouth of the tube being immersed in lime-water, contained in a watch-glass. The production of a white deposit of carbonate of lime will prove that the substance under examination, contained carbon. The oxygen of the oxide of copper or chromic acid, here serves as the medium for converting the carbon, present in the organic matter, into carbonic acid. If the *quantity* is required to be determined, then it will be necessary to connect the tube containing the mixture, with another tube, in which is placed powdered chloride of calcium (for the purpose of drying the carbonic acid), and conduct the products of combustion into a balanced vessel containing a saturated solution of potassa. (*See* ANALYSIS OF ORGANIC SUBSTANCES.) The amount of carbonic acid, and by calculation, the amount of carbon, present, may be thereby determined.

Two other forms of carbon require a brief notice.

Animal Charcoal.—Charcoal obtained by the carbonization of animal substances, such as muscle, horn, or hoof, resembles wood-charcoal in its general characters; but instead of retaining the form of the matter from which it is produced, it appears as if it had undergone fusion, and often has a peculiar lustre and sponginess. In all animal charcoals, we discover traces of nitrogen, derived probably from the presence of paracyanogen, or of mellone; they also contain the fixed saline and other bodies which existed in their respective sources. The charcoal obtained by the distillation of bone, is called *bone-black* and *ivory-black* in commerce, and is mixed with a large proportion of phosphate of lime and other earthy salts contained in the bone, so that for some purposes it requires to be freed from these salts by digesting it in diluted hydrochloric acid, and then washing and drying it. The special properties of animal charcoal in reference to the destruction of odors and colors, have already been mentioned. They are due to its molecular state, and not to difference of composition, charcoal being essentially the same under all its various forms. Of the different kinds of charcoal used for decoloration, bone charcoal or ivory-black, is comparatively feeble, although it is superior to wood-charcoal. Its decolorizing properties are nearly doubled by washing it with diluted hydrochloric acid, to remove the mineral matter, and afterwards with water. For perfect decoloration, the charcoal finely powdered, should be allowed to remain for some hours in contact with the colored liquid, and in certain cases warmed. The charcoal employed, should contain no substances soluble in water or in alcohol. After a time, animal charcoal loses its efficacy, the surface being covered with the coloring matter and other impurities, but the property may be restored by reheating it in close cylinders. This renovation is a necessary process in large sugar-refineries. We have found that a sample of good animal charcoal contained only 18 per cent. of carbon, leaving as a residue after combustion, 82 per cent. of phosphate and carbonate of lime.

Lamp-black is prepared principally by the combustion of refuse and residuary resin, left by the distillation of turpentine, as well as of the tarry oils obtained in the distillation of coal. These are burned in a furnace, so constructed that the dense smoke arising from it may pass into chambers hung with old sacking, where the *soot* is deposited, and from time to time swept off and sold without any further preparation. When lamp-black has been thus procured and heated red-hot, it may be regarded as a pure form of charcoal, for it burns entirely away, and leaves no residuary ash, but, it is found to contain traces of oxygen and hydrogen. A pure form of lamp-black for chemical purposes, may be obtained by burning camphor, and receiving the carbon of the smoke in a saucer or basin. When washed with alcohol this is pure carbon. A substance analogous to lamp-black is obtained by passing the vapor of certain oils, and of hydrocarbonous compounds, through red-hot tubes; at that high temperature they are more or less perfectly decomposed, and deposit a quantity of impalpable charcoal, in which, however, as in lamp-black, traces of hydrogen may be detected. Pure lamp-black, as it is procured from the carbonaceous smoke of the tarry oils from coal, is a very light flocculent substance. We found a sample of this carbon to yield only one per cent. of a white ash, whereas the substance ordinarily sold as lamp-black, yields an ash containing iron and silica, amounting to 9 per cent. of its weight. It is close and heavy, and appears to be a mixture of soot and finely powdered charcoal. One of the principal uses of lamp-black is in the manufacture of printers' ink. *Spanish-black* is the carbon of cork; *Vine-black*, that which results from vine-tendrils, and *Peach-black* from peach kernels; the two former have a brownish tint, and the latter a bluish tint. *German* or *Frankfort-black*, is said to be obtained by the carbonization of a mixture of grape and wine lees, peach kernels, and bone-shavings, and to be especially fit for copper-plate printing.

CARBON AND OXYGEN.—Although a powerful affinity exists between these bodies, they have no tendency to combine at ordinary temperatures. Carbon as it exists in certain organic compounds, exposed to the conditions of decay or putrefaction, will, however, unite with the oxygen of the air to form carbonic acid. Thus if damp and decaying woody fibre (sawdust) be kept in a closed vessel of air for some weeks, it will be found that the air will no longer support combustion, and that oxygen has been to a greater or less extent replaced by carbonic acid. It is probable that the union of carbon and oxygen here takes place as a result of evolution in the nascent state. When carbon is in a free state, it will not combine with oxygen below a red heat.

Chemists have enumerated eight compounds of these elements, two of which are gaseous, and are well known under the name of—1, *Carbonic oxide* (CO); and 2, *Carbonic acid* (CO_2). The other compounds are—3, *Oxalic acid* ($C_2O_3,3HO$), a crystallizable vegetable acid, which will be described hereafter, and its derivative, 4, the *Mesoxalic acid* (C_3O_4). In addition to these, there are four other compounds, possessing at present, but little chemical interest, and therefore requiring only a brief notice. These are only known in the hydrated or combined state. They are—5, the *Rhodizonic acid* ($C_7O_7,3HO$), so named from the red color of its salts. The rhodizonate of potassa is procured by digesting in water the compound of potassium and carbonic oxide, produced in the manufacture of potassium, or as a result of heating potassium in the gas. The acid may be procured from this salt; it is a solid crystalline acid forming colored salts. 6, *Croconic acid* (C_5O_4,HO). Croconate of potassa is a product of the decomposition of the rhodizonate of potassa, when this salt is boiled in water; the acid may be obtained from the solution of the croconate, by the addition of fluosilicic acid. It is a solid crystalline substance, of a yellow color, whence its name. 7, *Mellitic acid* (C_4O_3,HO). This is obtained by a complex process, from a mineral known as mellilite (honeystone), a mellitate of alumina. It is a solid colorless acid, crystallizing in prisms, and yielding by dry distillation, 8, *Pyromellitic acid* (C_5O_3); also a crystalline body, remarkable for its solubility in strong nitric and sulphuric acids, without change.

CARBONIC OXIDE. *Oxide of Carbon* (CO).—This gas was discovered by Priestley, but its real nature was first made known by Cruickshank, in 1802. It may be procured by gently heating oxalic acid with three times its weight of strong sulphuric acid, or a sufficient quantity of the acid to drench the crystals; the mixture effervesces in consequence of the evolution of carbonic oxide and carbonic acid gases: the latter may be separated by a solution of potassa, and pure carbonic oxide will remain. If the experiment be performed in a test-tube, the carbonic oxide may be burnt at the mouth of the tube. In this case the evolution of gases is caused by the abstraction of water from oxalic acid, which contains, in its anhydrous state, the elements of one atom of carbonic oxide and one atom of carbonic acid; but these can only exist as oxalic acid when in union with water, or with a base. Crystallized oxalic acid is$=C_2O_3,3HO$, which acted upon by three atoms of oil of vitriol $=3[SO_3,HO]$ become $3[SO_3,2HO]+CO_2+CO$; the hydrated sulphuric acid, darkened in color, remains in the retort. It may also be procured by heating, in an iron or earthen retort, a mixture of carbonate of lime (chalk) or baryta, with its weight of iron or zinc filings. The changes are as follows: $3BaO,CO_2+2Fe=3CO+3BaO+Fe_2O_3$, and $CaO,CO_2+Zn=CO+CaO+ZnO$. Chalk mixed with finely powdered charcoal, and heated to full redness, also yields this gas ($CaO,CO_2+C=2CO+CaO$). The first portions of gas being mixed with air, should be rejected. In all cases carbonic acid is also evolved; this may be separated by causing the gases to traverse a strong solution of potassa, or a tube containing broken pumice soaked in potassa. Carbonic oxide is not very soluble in water; hence it may be collected and preserved over water. The tests of its purity are that it should not give any precipitate with lime-water, or red fumes with deutoxide of nitrogen. This gas is a product of the combustion of carbon when the latter element preponderates, or the supply of oxygen is inadequate to the production of carbonic acid. The lambent blue flame which sometimes plays upon a coke or charcoal fire, or is seen to issue from certain furnaces, is carbonic oxide, produced by the passage of carbonic acid over red-hot charcoal, CO_2+C being converted into $2CO$.

Properties.—The specific gravity of this gas compared to hydrogen is as 14 to 1; and to atmospheric air as 0·9674 to 1·000; 100 cubic inches weigh 29·96 grains. Carbonic oxide is a powerful narcotic poison. When breathed it is speedily fatal to animals: it produces before death giddiness and insensibility, followed by profound coma. There can be but little doubt that some of the noxious effects hitherto attributed to carbonic acid, have been due to the action of this gas. It is produced during the combustion of any form of carbon when this element is in excess, and it may escape through leaks in stoves or flues. Leblanc found that an atmosphere containing only 1-100th of carbonic oxide was as fatal to a bird as one containing 1-25th part of carbonic acid. Boussingault has lately made the discovery, that this gas, with light carburetted hydrogen, in the proportion together of 3 or 4 per cent., is eliminated by the green parts of vegetables under the influence of water, light, and heat. This may arise from the decomposition of carbonic acid in vegetation, not being so complete as it has been hitherto supposed to be. If this observation be confirmed, it will show that while vegetation aids in purifying the air, it leads to the evolution of small quantities of one of the most deadly gases known to chemists; and differing from some other noxious gases in the fact that it cannot be recognized by its odor, or, in the small proportion in which it exists, by any other sensible properties. Aquatic plants and those growing in swampy places, evolve it in greater proportion than those growing on a dry soil (*Cosmos*, Nov. 22, 1861). Is this gaseous poison the secret cause of the unhealthiness of such localities?

Carbonic oxygen extinguishes flame and burns with a peculiar blue light when mixed with, or exposed to, atmospheric air. Thus, then, it is a combustible gas, but a non-supporter of combustion. When consumed in air it emits no odor, and there is no deposit of solid matter. Its volume is also unchanged; each cubic inch of carbonic oxide being converted into a cubic inch of carbonic acid ($CO+O=CO_2$). Its conversion into carbonic acid by combustion, may be proved by adding lime-water to a jar of the gas while it is in the act of burning. Sir H. Davy found that the temperature of an iron wire heated to dull redness was sufficient to inflame it. It has no taste, and little odor, and when pure, it occasions no precipitate in lime-water. If burned under a dry bell-glass of air or oxygen, no moisture whatever is deposited, showing that it contains no hydrogen.

Carbonic oxide suffers no change by being passed and repassed through a red-hot porcelain tube; it is not decomposed at high temperatures by phosphorus, sulphur, nor even, according to the experiments of Saussure, by hydrogen (*Journal de Physique*, lv.), although it is stated, upon other authorities, that at high temperatures, hydrogen does decompose it. When one volume of carbonic oxide is detonated with one of protoxide of nitrogen, there result one volume of carbonic acid and one of nitrogen ($CO+NO=CO_2+N$). None of the metals exert any action upon this gas, except potassium and sodium, which, at a red heat, burn in it by abstracting its oxygen, and carbon is deposited. In the nascent state, it forms a solid compound with potassium, from which rhodizonic and croconic acids may be obtained (p. 244). It appears to combine with this metal at a temperature not exceeding 176°. At the melting-point of potassium the gas is absorbed, forming a black mass, which is spontaneously inflammable in air (Liebig).

Carbonic oxide is one of the few compound gases which has not yet been liquefied by the most intense cold and pressure (p. 74). The gas is a perfectly neutral oxide. If pure, it neither reddens nor turns green, the blue infusion of cabbage. Water dissolves about 6 per cent. of the gas by volume: it is not soluble in a strong solution of potassa. Berthelot found that the gas was slowly dissolved by hydrochloric acid, or by ammonia holding in solution subchloride of copper. Carbonic oxide is a powerful deoxidizing agent, inasmuch as it always has a tendency, at a high temperature, to be converted into carbonic acid. It thus plays an important part in blast-furnaces in the smelting of iron. At a red heat, it converts the alkaline and alkaline-earthy sulphates to sulphides, $CaO,SO_3+4CO=4CO_2+CaS$. Levol has recommended a solution of chloride of gold as a test for the gas, inasmuch as it reduces this metallic compound at common temperatures; but sulphurous acid has also this property. Oxalate of lime, for a similar reason, serves as a flux for the reduction of arsenious acid. When carbonic oxide is added in an equal volume, to a mixture of hydrogen and oxygen gases in explosive proportions, it prevents spongy platinum from causing detonation; but the gases slowly react upon each other, and form water and carbonic acid.

Composition.—The composition of carbonic oxide is determined by the result of its combustion with oxygen, with which it forms carbonic acid. When two volumes of carbonic oxide and one of oxygen are acted on by the electric spark, detonation ensues, and two volumes of carbonic acid are produced: hence it follows, that carbonic oxide is unchanged in volume by this conversion, and that it contains half as much oxygen, and the same quantity of carbon, as carbonic acid. Hence, assuming carbonic oxide to be a protoxide of carbon, it will consist of—

	Atoms.	Weights.	Per cent.	Vols.	Sp. Gr.
Carbon . . .	1	6	42·85	1	0·4146
Oxygen . .	1	8	57·15	½	0·5528
	1	14	100·00	1	0·9674

The volume of carbon-vapor which has not been determined experimentally, is here assumed to be equal to that of hydrogen. As carbonic oxide has a sp. gr. of 0·9674, and it contains half its volume of oxygen, then 0·9674 —0·5528(1·1057÷2)=0·4146, the hypothetical sp. gr. of carbon-vapor.

From this result, the percentage of carbon and oxygen contained in the gas, may be easily deduced; for 0·9674 : 0·4146 : : 100 : 42·85 per cent. of carbon. The difference will represent the oxygen. Carbonic oxide has the sp. gr. and equivalent of nitrogen.

Chlorocarbonic Acid; Phosgene Gas (CO,Cl).—This gas may be obtained by exposing to solar light a mixture of equal volumes of chlorine and carbonic oxide: hence its name (φῶς, *light*, γενναω, to *produce*). It is also formed by exposing the mixed gases to ordinary daylight, but several hours are required for the purpose. When perfectly excluded from light, the gases exert no mutual affinity. In the sunshine the mixture diminishes in bulk to one-half of its original volume, and forms a compound of a peculiar and pungent odor, but not disagreeable when considerably diluted. It reddens litmus, and is resolved by water into carbonic and hydrochloric acid gases. Alcohol and pyroxylic spirit absorb it, and form ethereal compounds. The specific gravity of chlorocarbonic acid to hydrogen is as 50 to 1, and to common air as 3·425 to 1. In reference to the theory of substitutions this compound has been regarded as carbonic acid, in which 1 equivalent of oxygen has been replaced by 1 of chlorine.

CARBONIC ACID. *Fixed Air; Aerial Acid* (CO_2).—This compound was first described by Dr. Black, in 1757, under the name of fixed air, a name which it derives from its being a constituent of limestone. Its composition was first determined by Lavoisier. It is produced by burning carbon, either pure charcoal, graphite, or the diamond, in oxygen gas; the oxygen, in thus becoming converted into carbonic acid gas, suffers no change of volume. When charcoal is burned in a jar of oxygen gas the phenomena of combustion depend upon the nature of the charcoal, which, if well made, and of a dense wood, glows with intense heat without flame, and gradually disappears; but if of a lighter wood, and especially if covered with portions of the bark, it throws off jets of brilliant sparks. These scintillations are especially brilliant and beautiful, when a small piece of the charred bark of oak or elm is used; it should be attached to a copper wire, and introduced into a sufficiently capacious air-jar filled with pure oxygen; the combustion may thus be made to last for some minutes. If only the quiet combustion of charcoal is required for the purpose of showing the conversion of oxygen into carbonic acid, the best kind of carbon which can be used for this purpose is that obtained from box, lignum vitæ, or other hard and dense woods.

Carbonic acid is, like sulphurous acid, an anhydrous oxacid gas, having less affinity for bases than sulphurous acid, so that it may be expelled from the dry alkaline carbonates by means of this gas. It is a natural constituent of the atmosphere, of which it forms from $\frac{1}{2000}$th to $\frac{1}{2500}$th part: it is a result of the decomposition of animal and vegetable substances, and is the chief gaseous product of combustion, respiration, and the vinous fermentation.

Preparation.—Carbonic acid constitutes about half the weight of carbonate of lime or marble. It is readily procured by adding to one part of broken marble one part of hydrochloric acid diluted with three parts of water. The gas is instantly evolved, producing the phenomenon known as effervescence ($CaO,CO_2+HCl=CO_2+CaCl+HO$). A flask or retort may be used in the experiment. The gas should not be collected until a few bubbles of it, thrown into a jar containing deutoxide of nitrogen, cease to produce ruddy fumes. It may be collected in a water-bath, although, owing to the solubility of the gas in water, there is considerable loss. One grain of pure marble will give nearly a cubic inch of the gas.

Properties.—This gas is colorless, of a slightly sour taste, and much heavier than atmospheric air, its specific gravity being about 1·52. Compared with hydrogen, its sp. gr. is as 22 to 1. 100 cubic inches weigh 47·087 grs. at mean temperature and pressure. When so far diluted with air as to admit of being received into the lungs, carbonic acid operates as a narcotic poison, producing drowsiness, entire loss of muscular power, rapidly followed by insensibility and coma. When the gas is respired in the lowest poisonous proportion, the symptoms come on very gradually, and the transition from life to death is usually tranquil. This gas is the fatal *choke-damp* of coal mines. It is a product of the combustion of light carburetted hydrogen (fire-damp), and is the common cause of death to miners who are not at once killed by the explosion.

It is not combustible, and immediately extinguishes other bodies which are in a state of combustion. This may be proved by successively introducing into a jar of the gas a burning taper, a piece of ignited camphor, and a large flame of ether, on cotton or tow. The flames of these substances are instantly extinguished. We have found that a candle will burn in mixtures of carbonic acid and air until the proportion of the gas reaches 20 per cent.; but such mixtures would be noxious to respire: hence, although the extinction of a candle in wells or cellars is a proof of danger, the fact that it continues to burn must not be regarded as an indication of safety. We have also found that the presence of a large proportion of oxygen completely counteracts this effect of carbonic acid. In a mixture of equal parts of oxygen and carbonic acid a taper burns as brilliantly as in oxygen; and the presence of carbonic acid would not be suspected in the mixture but for the effect produced by the addition of lime-water and other tests. Carbonic acid cannot, however, replace nitrogen in air. When it forms four-fifths of the mixture, combustion is no longer supported, and animals are killed.

This gas possesses well-marked acid properties. If blue infusion of litmus is added to a jar of the gas, it is speedily reddened. If the red liquid is boiled, the blue color will be restored, thus showing that the reaction depended on a gaseous acid. If to jars of the gas, solutions of lime, baryta, or subacetate of lead, be separately added, dense white precipitates of the respective carbonates of these bases, will be produced. Lime-water is the usual test for this gas, but a solution of the subacetate of lead is more delicate in its reaction. Lime-water will be found to be alkaline to test-paper before pouring it into the gas, but it will entirely lose its alkalinity afterwards. Air containing one per cent. of carbonic acid produces a milkiness in lime-water, hence in an atmosphere containing a noxious proportion of carbonic acid, lime-water is instantly rendered turbid, even by a small portion of the air collected in a bottle. If the precipitated carbonate of lime be transferred to another jar of carbonic acid, it will be found after a time to be re-dissolved. Carbonic acid is absorbed by alkalies. If a saturated solution of potassa is put into a jar of the gas, and well shaken, the plate-glass cover of the jar is fixed as if by a vacuum. On removing the cover and introducing a lighted taper, this will be found to burn as in air. Introduce into a wide jar, containing carbonic acid, some solid hydrate of potassa with a small quantity of water. Cover quickly the mouth of the vessel with a stout layer of caoutchouc, and then agitate the liquid. As the carbonic acid is absorbed by the dissolved potassa, the atmospheric pressure forces down the elastic caoutchouc cover, just as in a vessel exposed to the vacuum of an air-pump. The most perfect vacua known, are now produced by gently heating hydrate of potassa in tubes filled with pure carbonic acid, hermetically sealed.

Solution.—Water takes up its own volume of the gas at common temperature and pressure, and acquires a slight increase of specific gravity (about

1·0018). Under increased pressure a much larger quantity is absorbed. Thus, water may be made to take up five or six times its volume by pressure. It then becomes brisk and tart, and reddens vegetable blues. If litmus-paper, thus reddened, be exposed to the air, the blue color returns as the acid evaporates. By freezing, boiling, or exposure to the vacuum of an air-pump, the gas is given off, and it gradually makes its escape when exposed to air, collecting in small bubbles upon the sides of the containing vessel, and passing off with especial rapidity when any foreign substances are thrown in, or when any substance is dissolved in the water; thus it is, that sugar added to soda-water, cider, champagne, or other similar carbonated liquors, occasions in them an immediate and abundant effervescence. The effervescent qualities of many mineral waters, as well as of fermented liquids, are referable to the presence of this gas. Artificially *aërated waters* are prepared on a large scale by condensing carbonic acid under pressure, into water holding dissolved alkaline or saline substances. Carbonic acid may be thus made to dissolve lime, magnesia, and the protoxide of iron. A solution of carbonic acid in water, precipitates lime-water, but re-dissolves the precipitate when added in larger quantity.

Carbonic acid forms no hydrate with water; and when liquefied, or solidified by cold, it will not combine with water. Some English chemists have given to it the name of *Carbonic anhydride.* As this term is applied to acids which are capable of forming definite hydrates with water, in order to distinguish the anhydrous from the hydrated state, it is singularly inappropriate to apply it to an acid which forms no hydrate whatever. The words, too, imply, not the absence of water, but the absence of *hydrogen.* Nitrogen and carbonic oxide would, in either point of view, have an equal claim to be called anhydrides. Long established usage has fixed the name of carbonic acid in chemical nomenclature, and no sufficient reason has been adduced for the adoption of this innovation.

As all common combustibles, such as coal, wood, oil, wax, and tallow, contain carbon as one of their component parts, so the *combustion* of these bodies is always attended by the production of carbonic acid. Float a lighted taper, fixed in a cork, on lime-water, contained in a glass dish; and invert over the taper, a bell-glass of air or oxygen. After a time, the taper will be extinguished, and the surface of the lime-water will be covered with a white film of carbonate of lime. Hold a large jar so that its mouth shall be slightly above a jet of burning gas, or the flame of a spirit-lamp. After a few minutes, remove it, and pour lime-water into the jar. This will be rendered milky by the carbonic acid which has resulted from combustion.

This gas is also produced by *respiration;* hence it is detected, often in considerable proportion, in crowded and illuminated rooms which are ill-ventilated. The symptoms produced by the respiration of such a contaminated atmosphere, are difficulty of breathing, giddiness, and faintness. Its expiration from the lungs is easily shown, by blowing the expired air through lime-water by means of a small tube; the liquid becomes milky, and soon deposits carbonate of lime The same fact is also strikingly shown by allowing expired air to pass into a solution of chloride of lime, colored blue by litmus. The color is soon destroyed by the carbonic acid discharged from the lungs decomposing the chloride, and setting free chlorine. An apparatus has been contrived, by which the air inspired, is made to traverse lime-water without producing any change in it, while the air expired through the same liquid, produces carbonate of lime. If lime-water is placed in a large jar, and the air of the jar is breathed two or three times, taking care that the air, as it is expired, is returned into the jar, the lime-water, which was unaffected by the air contained in the vessel, will be rendered milky from the production of carbonate of lime. Inspired air contains only 1-2000th part of carbonic acid, but expired air contains (on the assumption that 3 per cent. only are present) sixty times as much carbonic acid, or 1-33d part by volume. Dr. Prout assigns the proportion of carbonic acid in expired air at from 3·3 to 4·1 per cent., and the average at 3·43 per cent. It varies at different periods of the day, according to the state of health, and other conditions. On this estimate, however, 16 cubic inches, representing 4 grains of solid carbon, are thrown out of the lungs of an adult every minute—a quantity amounting to about 12 ounces of carbon in 24 hours! According to Dr. Brinton (*Food and its Digestion*), the carbonic acid daily given off from the adult healthy body may be estimated at 17 cubic feet, or about two pounds in weight. Allowing that half a cubic foot (about an ounce) is eliminated through the skin, the remainder is exhaled from the lungs. The quantity of carbon or charcoal by weight, to which this amount of carbonic acid would correspond, is *nine ounces.* In making this estimate Dr. Brinton assumes 1-2500th part of carbonic acid as the proportion present in *inspired*, and 1-25th part as the proportion contained in *expired* air.

Carbonic acid retards the putrefaction of animal substances. It favors the growth and development of vegetables in air and water. Most plants thrive in an atmosphere containing as much as a tenth or twelfth part of carbonic acid; and under certain circumstances they decompose it, and evolve oxygen.

At high temperatures, carbonic acid is decomposed by carbon and several of the metals, and is converted into carbonic oxide. The influence of ignited carbon in effecting this decomposition is seen in an ordinary coal-fire. The oxygen of the air in passing between the bars below, produces carbonic acid: and this is deoxidized by the red-hot coke ($CO_2+C=2CO$), the carbonic oxide thus produced, burning at the top of the fire with a flickering blue flame. Potassium and sodium, when heated intensely, burn in the gas, and are converted into potassa and soda, whilst the carbon of the gas is separated in the form of charcoal. There are some other substances which, at high temperatures, are capable of decomposing carbonic acid, and abstracting part of its oxygen; thus, if a mixture of 2 parts of hydrogen and 1 of carbonic acid by volume, be passed through a red-hot tube, water and carbonic oxide, with the excess of hydrogen, escape.

Carbonic acid is not affected by heat alone; it may be passed through a red-hot porcelain tube unchanged; but it is partially converted by a succession of electric sparks into carbonic oxide and oxygen. It is worthy of remark, as illustrative of the variable effects of the electric spark, that by means of it, a mixture of carbonic oxide and oxygen may be suddenly converted into carbonic acid. Iron, zinc, and manganese, at a high temperature, deprive the gas of half of its oxygen, and convert it into carbonic oxide.

Equivalent and Tests.—The equivalent or atomic weight of carbonic acid is 22, and its volume-equivalent is 1. The tests for its presence are—1, the extinction of a burning taper; 2, the production of a milky precipitate of carbonate of lime, when lime-water is added to a jar containing the gas; 3, entire absorption and removal by potassa. For this purpose, the carbonic acid should be collected in a tube over mercury, and some portions of solid potassa, with a small quantity of water, introduced. The carbonic acid slowly disappears, and if the gas be pure, there will be no residue. A strong solution of potassa, or portions of alkali, moistened, and placed in an appropriate apparatus, previously balanced, will separate carbonic acid from most neutral gases; and by the increase in the weight of the potassa, a chemist will be enabled to determine the weight or volume of carbonic acid present.

Composition.—As oxygen, in being converted into carbonic acid by the combustion of carbon, undergoes no change of volume, it is evident that the weight of carbon present must be equal to the difference between the specific gravities of carbonic acid and oxygen=0·4145 (1·5202—1·1057). Assuming that this represents one volume of carbon-vapor, then the weight of carbon in 100 parts of carbonic acid is equal to 27·22 (1·520 : 0·4145 : : 100 : 27·22), and the oxygen will be, 72·78. These elements are obviously in the proportions of 3 to 8, or 6 to 16, as found by Stas and Dumas in the burning of pure carbon in oxygen, and in taking directly the weight of the resulting carbonic acid. The composition of this gas will therefore stand as follows:—

	Atoms.	Weights.	Per cent.	Vols.	Sp. Gr.
Carbon	1	6	27·22	1	0·4145
Oxygen	2	16	72·78	1	1·1057
	1	22	100·00	1	1·5202

As the weight of carbon is added to that of the oxygen without altering its bulk, this gas is very heavy; hence it accumulates temporarily in wells, cellars, or other excavations in the soil; but unless constantly produced, it will soon disappear by the law of diffusion (p. 79). The following experiments will serve to prove how much denser it is than air. Balance a glass shade in a scale pan, allow a current of carbonic acid gas to pass into it from a bottle, taking care that the tube conveying the gas reaches nearly to the bottom of the shade. It will collect and displace the air, and the shade will now preponderate by reason of the greater weight of the gas. A lighted taper lowered within the shade is extinguished. Dry nitre paper ignited, will also be extinguished when introduced, but the smoke produced as a result of its combustion will float upon the stratum of carbonic acid. A soap-bubble, or a small collodion balloon of air, will also float upon the gas. If a small jar or glass-beaker is lowered into the shade, it will, in a few minutes, be filled (by displacement) with carbonic acid, which may be removed to a distance and tested by a lighted taper, as well as by lime-water. Remove the covers from two small jars containing the gas, taking care that one is placed with its mouth upwards and the other with its mouth downwards. After a few minutes, a lighted taper may be applied to the two. It will be found that the gas has fallen out of the jar with its mouth downwards, and that the taper will burn brightly in it; whereas it will be immediately extinguished in the other jar, and will not entirely escape from it for a quarter of an hour, or longer. Smoke produced by the combustion of nitre-paper at the mouth of the jar, will float like a cloud upon it. The falling of the gas from one vessel to another may be easily demonstrated by allowing a taper to burn at the bottom of a jar of air, and then gradually inverting over it another jar containing carbonic acid: the taper will be extinguished in the jar which contained air, while in that which contained the carbonic acid it will now continue to burn. This experiment may be varied by placing three lighted tapers at different levels in a glass basin about eight inches wide, and five or six inches deep. If a large jar of carbonic acid is brought over the mouth of the basin, at the part corresponding to the lowest taper, and the cover gradually raised, the gas will fall through the air in the basin, and as it rises it will successively extinguish the three tapers. The Grotta del Cane, near Naples, is an excavation on the side of a hill, in which carbonic acid collects, owing to the basin-like form of the floor of the grotto. The gas is always issuing from fissures in the soil, and thus the accumulation goes on faster than the diffusion. Dogs are asphyxiated by being held within the stratum of gas, which rises to about the height of the knee. On gradually lowering burning straw and phosphorus in this grotto, we found that the level of the gas was accurately determined by the extinction of the flame and the floating of the smoke. These well-known facts regarding the specific gravity of carbonic acid, have led to the erroneous supposition that, under all circumstances, the gas will accumulate, and remain on the floor or soil. The law of diffusion, however, prevents such accumulation, unless there is a constant source from which the gas can proceed.

Liquid and solid Carbonic Acid.—Carbonic acid may be liquefied by great pressure, aided by a low temperature (page 74). It is usually liquefied by its own pressure—*i, e.*, by liberating it in a wrought-iron vessel, the capacity of which is very small compared with the amount of gas which can be set free by the action of an acid on bicarbonate of soda. It may be *liquefied* by mere cooling to 106° without pressure. The *liquid* is colorless, very soluble in alcohol, ether, and essential oils. It will not mix or combine with water, but floats on that liquid. It does not redden solid extracts of litmus. It dissolves camphor and iodine. Although it has no solvent action on gutta percha or caoutchouc, it penetrates into these substances, and whitens them. It is a strong insulator of electricity, and is deoxidized only by the alkaline metals. (Gore, *Proc. R. S.*, 1861, No. 43, page 85.)

By allowing liquefied carbonic acid to escape through a perforated metallic box, the cold produced is so intense that a portion of the gas is solidified, and presents the appearance of a snowy-looking mass. *Solid* carbonic acid has a temperature of at least 100° below zero, but it is surrounded in the air with a gaseous atmosphere, which prevents immediate contact with bodies, and it rapidly disappears as gas, when exposed. This solid acid may be borne in the hand without any particular sensation of coldness or pain; but when mixed with ether, it produces an intense degree of cold, which would destroy at once the vitality of any part of the body with which it was in contact. A small portion placed on stout plate-glass produced no effect until ether was poured upon it, when, owing to the intense cold suddenly produced, the glass was broken to pieces. A sheet of paper was folded so as to make a long trough, or cavity, into which liquid mercury was poured; the metal was then covered with solid carbonic acid, and ether was poured upon it. The mercury was instantly frozen into a long bar of metal, the temperature of the air being at the time above 60°. Medals of mercury have thus been made, and preserved for some time in the cold bath of carbonic acid and ether. Gases may be liquefied and solidified by means of this bath. *In vacuo* the cold produced by it has been calculated by Faraday to reach to —166°, or 198° below the freezing-point of water.

Carbonates.—These salts are represented by the formula MO,CO_2, and the bicarbonates by $MO,2CO_2$. Among the alkaline carbonates those of potassa, soda, ammonia, and lithia, are alone soluble in water, and have an alkaline reaction. Those of lime, magnesia, protoxide of iron, and manganese, are dissolved by water containing much carbonic acid. A *soluble* carbonate gives a white precipitate with the solutions of lime, or baryta, or with their salts. This precipitate is dissolved with *effervescence* (escape of carbonic acid) by the acetic and other acids. The precipitate given by sulphate of magnesia is soluble in hydrochlorate of ammonia, containing free ammonia; that given by lime is not. A soluble *bicarbonate* gives no precipitate with sulphate of magnesia, and a yellowish (becoming slowly a red) precipitate, with a solution of corrosive sublimate. This test at once precipitates a soluble carbonate, excepting that of lithia, of a deep-red color. A solution of a carbonate added to a strong acid, effervesces strongly. *Insoluble* carbonates are identified by their dissolving with effervescence in nitric acid. The gas which escapes is invisible, and without smell. It precipitates lime-water.

CHAPTER XX.

CARBON. COMPOUNDS OF CARBON WITH HYDROGEN, NITROGEN, CHLORINE, AND SULPHUR.

CARBON AND HYDROGEN.—These elements unite in several proportions, forming gaseous, liquid, and solid compounds, among which it is sometimes difficult to distinguish those which ought to be considered as definite, from others which are mere mixtures. These compounds are generally termed *hydrocarbons*, or *carbo-hydrogens*. Amongst them are some striking illustrations of that species of isomerism, which has been called *polymerism* (page 19)—that is, of compounds differing, often essentially, in their physical or chemical properties, or both, and yet apparently produced by the union of the same elements in similar proportions. Among these compounds, may be mentioned the oils of lemon, turpentine, juniper, and savin; naphtha, naphthaline, and benzole; all remarkable for their inflammability and their combustion with a yellowish-white smoky flame. As these hydrocarbons are of a complex nature, and are for the most part educts, or products, of organic substances, they will be the subject of consideration hereafter. The three which now require notice are, the light carburetted hydrogen, CH_2, olefiant gas, C_2H_2, and oil gas, C_4H_4.

LIGHT CARBURETTED HYDROGEN (CH_2).—*Marsh-gas. Fire-damp.*—This gas is considered to be diffused in very small proportion in the atmosphere. It is the well-known *Fire-damp* of coal-mines, rushing out occasionally in enormous quantities in "blowers" from seams of coal, owing to its being probably contained in the strata under high pressure. It derives its synonym of *marsh-gas* from the fact that it is formed in stagnant pools in hot weather, during the spontaneous decomposition of vegetable matter. It may be procured by stirring the mud, and collecting the gas as it rises in bubbles, in a glass-jar filled with water and inverted. In this state it is mixed with nitrogen and carbonic acid; the latter may be separated by washing the gas in lime-water or in a solution of caustic potassa. The gas procured from a *blower* in a coal mine, after having been washed with lime-water, furnishes this compound in a pure state. It may also be obtained by the decomposition of certain acetates, when heated in a retort with an excess of alkali. Dumas recommends for this purpose 40 parts of crystallized acetate of soda, 40 of caustic potassa, and 60 of powdered quick-lime. They should be strongly mixed and well heated, the use of the lime being to prevent the action of the alkali upon the glass. At a heat approaching to dull redness, the gas is abundantly evolved, and may be collected over water; the action is determined by the affinity of the alkaline bases for carbonic acid, and the instability of the acetic acid at high temperatures; an atom of acetic acid and an atom of water produce carbonic acid, which combines with the soda and potassa; while light carburetted hydrogen passes off; ($C_4H_3O_2+HO$) yielding $2CO_2$, and $2CH_2$.

Properties.—The specific gravity of this gas is 0·552, and compared with hydrogen it is as 8 to 1. 100 cubic inches weigh 17·12 grains. It is a colorless gas. Its refractive power is 2·097, air being 1·000. When breathed in a pure state, it is fatal to life, but it is not very noxious when mixed with air, even when it forms from 8 to 10 per cent. of the mixture. It is sparingly soluble in water, and is not dissolved by fuming sulphuric acid. It does not support combustion, but is inflammable, burning with a pale yellowish flame, and producing carbonic acid and water $CH_2+O_4=CO_2+2HO$; it has, when quite pure, neither odor nor taste. It is not decomposed by the electric spark; but when passed through a white-hot tube, it deposits a portion of its carbon, $CH_2=C+H_2$. When chlorine is mixed with the pure gas, there is no immediate action; but when 1 volume of the gas and 3 of chlorine are mixed and exposed to diffused light, a violent explosion soon ensues, hydrochloric acid is formed, and carbon is deposited. One volume of the gas with two volumes of chlorine, produce the strongest effect ($CH_2+2Cl=2HCl+C$), and the combination is immediately effected by the electric spark. When the gas is previously mixed with its volume of carbonic acid, the chlorine may be added without danger. If exposed to light, carbonic acid is produced, and an oily liquid is deposited, which is chiefly bichloride of carbon (C,Cl_2). In the dark, there is no combination. When the gas is passed with chlorine through a red-hot tube, carbon is deposited, and hydrochloric acid is formed. When mixed with twice its volume of oxygen, and the mixture is detonated, it produces its volume of carbonic acid, and water is at the same time condensed. From these results, its constitution may be determined. One volume of oxygen is contained in each volume of carbonic acid; and as two volumes are required for the perfect combustion of the gas, the other volume of oxygen must combine with two volumes of hydrogen to form water, or

$$\underbrace{CH_2}_{\text{1 vol.}} + \underbrace{O_4}_{\text{2 vols.}} = \underbrace{CO_2}_{\text{1 vol.}} + \underbrace{2\,HO}_{\text{2 vols.}}$$

hence one volume of carbon-vapor and two volumes of hydrogen must be contained in each volume of the light carburetted hydrogen. Its specific gravity is in accordance with this constitution:—

	Atoms.	Weights.	Per cent.	Vols.	Sp. Gr.
Carbon	1	6	75	1	0·4146
Hydrogen	2	2	25	2	0·1382
	1	8	100	1	0·5528

The ascertained specific gravity is very nearly in accordance with this view, being 0·556.

The production of the gas in marshy localities, is owing to the decay of vegetable matter, and the decomposition of woody fibre, in contact with the elements of water. The water simply furnishes hydrogen and oxygen to the carbon of the decaying vegetables.

Coal Gas.—Gas procured by the distillation of bituminous coal in iron retorts, when it has undergone purification, consists chiefly of light carburetted hydrogen. 100 parts of coal, distilled at a high temperature, yield the following solid, liquid, and gaseous products by weight:—

Coke	68·93	Olefiant gas	0·78
Tar	12·23	Sulphuretted hydrogen	0·75
Water	7·40	Hydrogen	0·50
Light carb. hydrogen	7·04	Ammonia	0·17
Carbonic oxide	1·13	Nitrogen	0·03
Carbonic acid	1·07		

(Bunsen and Playfair).

One pound of cannel coal will yield four and a half cubic feet of gas. The carbonic acid is removed from the gaseous mixture by passing it through lime, and the sulphuretted hydrogen by causing it to traverse beds of hydrated oxide of iron and sawdust (page 212), and the ammonia by water. The purified coal gas, thus obtained, when not over-heated, was found to consist in 100 parts of 82·5 parts of light carburetted hydrogen and 13 of olefiant gas, with 3·2 parts of carbonic oxide and 0·3 of nitrogen. Its sp. gr. was 0·65. These were the proportions in the early stage of the process. The gaseous mixture collected after five hours' working, when the tubes had become strongly heated, contained a larger proportion of free hydrogen, derived from the decomposition of the light carburetted hydrogen. It then consisted in 100 parts, of 56 parts of light carburetted hydrogen and 7 of olefiant gas, 11 of carbonic oxide, to 7 of nitrogen and 21·3 of hydrogen. Its sp. gr. was 0·50. After ten hours' distillation, the olefiant gas had entirely disappeared—the light carburetted hydrogen amounted to only 20 parts, carbonic oxide 10, nitrogen 10, and hydrogen 60, the sp. gr. being as low as 0·345. (MITSCHERLICH.) The constitution of the coal gas varies, therefore, greatly with the temperature of distillation.

Coal gas is colorless, and has commonly a strong odor of naphtha vapor. A taper plunged to the bottom of a jar containing it, is extinguished; but the gas burns, where it meets with air, with a yellowish flame. Aqueous vapor is condensed on the sides of the jar, and carbonic acid may be proved to be a product of its combustion, by pouring lime-water into the jar, while the gas is burning; or by holding the mouth of a clean jar of air over a jet of gas in combustion, and then adding lime-water; the presence of carbonic acid will be indicated by a white precipitate. This gas may be kindled in air by a full red heat without flame. Apply a red-hot bar of iron to a jar of the gas, or to a current of gas, as it issues from a jet, and it will be found that the iron, although visibly red, will not inflame the gas unless the metal is heated to bright redness. If fine platinum wire is made red-hot in a gas-flame, as it is burnt with air from a wire-gauze burner, and the flame is suddenly extinguished, the wire will continue to glow in the current of unignited gas, causing the slow combustion of the gas and air without inflaming the mixture, until some portions of the wire acquire a white heat: the mixture is then suddenly kindled with a slight explosion. This gas is so light that the series of experiments described under hydrogen (page 110) may be readily performed with it. A jar of the gas may be removed from the water-bath, with its mouth downwards, without a cover, to a distance, and there ignited. It rapidly escapes from jars which are open with their mouths upwards. A jar of air held over a jar of the gas, suddenly uncovered, will thus receive it in the act of ascending. The contents may be exploded, while the jar which originally contained the gas, will contain air. Nitre-paper burnt at the mouth of an inverted jar of the gas will produce smoke, which will remain at the lowest level, the gas floating on the top of it. A jar opened under a balanced shade, inverted, will cause the opposite scale to preponderate, the air being displaced by the light gas which rises to the upper part of the shade. Soap-bubbles blown with this gas will ascend in air, and balloons of goldbeater's skin filled with it acquire great buoyancy, thus illustrating the principles of aërostation. As this gas is only half the weight of air, and only one-third the weight when partially decomposed by over-heating, it is now exclusively employed for the purposes of aërostation—the larger size of the balloon compensating for the higher specific gravity of the gas compared with hydrogen. Coal gas should have no acid reaction on infusion of blue litmus. If it contains sulphuretted hydrogen, it will give a brown discoloration to paper wetted with a salt of lead: if ammonia be present, this will be indicated by its restoring the color of faintly reddened litmus-paper. When these impurities coexist, the gas will give a bluish or pinkish red color to a solution of nitro-prusside of sodium. In spite of all ordinary methods of purification, coal gas, in burning, evolves an acid vapor, which is found to be sulphurous acid. This proceeds from a minute portion of sulphide of carbon vapor, which the common purifiers do not remove.

The illuminating power of coal gas is increased by saturating it with coal naphtha. The gas is simply passed through a box in which the vapor of naphtha is diffused, and it is speedily saturated with it.

In reference to *explosions in coal-mines*, two important chemical questions present themselves for consideration—1st, the proportion per cent. of light carburetted hydrogen, which forms the most dangerous explosive mixture with air; and 2d, the temperature at which such a mixture is liable to be kindled. It is here assumed that the gas is pure, and that it contains no admixture of olefiant gas or carbonic oxide. In the experiments which Davy performed on this subject, he found that the greatest explosive power was manifested when the gas was in the proportion of one volume to seven or eight volumes of air, or when it formed from 12 to 14 per cent. of the mixture. As two volumes of oxygen are theoretically required, and these correspond to ten volumes of air, it will be seen that the maximum explosive effect takes place with a smaller proportion of oxygen than theory indicates. When the gas was in the proportion of 20 per cent. of the mixture, there was combustion without explosion. When it amounted to rather less than 7 per cent., there was no explosion, but an enlargement of the flame of a candle; and this enlargement, but a diminishing ratio, was observed in mixtures gradually reduced to 3 or 4 per cent. of the gas. From these results, which have been since confirmed by the observations of others, it is obvious that long before the point of danger is reached, a warning is given by an elongation of the flame of a lamp or candle.

As to the temperature required for the explosion of a mixture of fire-damp and air, Davy observed that well-burned charcoal, ignited to the strongest red heat, did not explode any mixture of air and of the fire-damp; and a fire made of well-burned charcoal, *i. e.*, charcoal that burned without flame, was blown up to full redness by an explosive mixture containing the fire-damp, without producing its inflammation. An iron rod at the highest degree of red-heat, and even at the common degree of white-heat, did not inflame explosive mixtures of fire-damp; but, when in brilliant combustion, it produced this effect. Flame of any kind exploded a mixture of fire-damp and air. In reference to combustibility, therefore, this compound differs from the other common inflammable gases. Davy found that olefiant gas which explodes when mixed in the same proportion with air, is fired by both charcoal and iron heated to redness. Carbonic oxide, which explodes when mixed with two parts of air, is likewise inflamed by red-hot iron and charcoal; and hydrogen, which explodes when mixed with three-sevenths of its volume of air, takes fire at the lowest visible heat of iron and charcoal; this also occurs with a mixture of air and sulphuretted hydrogen.

The *safety-lamp* contrived by Davy for the prevention of accidents by explosion in coal-mines, consists of a cylinder of metallic wire-gauze containing from 700 to 900 meshes in the square inch. This presents a large metallic surface favorable for the cooling of flame, and of reducing its temperature below that required for kindling explosive mixtures. The principle of its operation may be illustrated by various experiments. Flame is nothing more than gaseous or vaporous matter, heated to a very high temperature, and requiring a high temperature for its continuance. (*See* page 97.) The following experiments will serve as illustrations: Place a lump of camphor on a sheet of wire-gauze like that which is used for the safety-lamp. The camphor may be inflamed from beneath, and it will there be consumed, but the inflammable vapor of the camphor will not be ignited above the gauze—the heat conducted by the metal having lowered the temperature far below that required for its combustion. A piece of tow soaked in ether or alcohol may be substituted for the camphor with like results. There will be no ignition of the vapor of either liquid above the gauze, while it will burn readily below. Into a small cylinder of wire-gauze (closed at the bottom with a layer of gauze, but open at the top) throw a mass of tow soaked in alcohol and inflamed. The cylinder may now be placed in a saucer containing alcohol. The whole of the spirit will be drawn in and consumed within the cylinder; but there will be no inflammation of that which is on the outside. Let the same cylinder be fitted closely to a wire-stand supporting a wax taper, so that when the taper is kindled, it may be completely inclosed by the gauze-cylinder. If a jar of hydrogen or coal-gas, or a mixture of either with air, be brought over the cylinder inverted, and very gradually lowered, the inflammable gas will traverse the gauze and burn with flame, but without explosion, in the interior of the cylinder, and there will be no kindling of the explosive mixture on the outside of the cylinder. In this manner the whole of the inflammable gas may be consumed without being inflamed in the jar; whereas, if any such mixtures were brought over the lighted taper, not covered by the gauze-cylinder, there would be instantaneous inflammation and explosion.

The safety-lamp consists of an ordinary oil-lamp, to which a gauze-cylinder is so secured as to allow of combustion only by the air which traverses the meshes of the gauze. As a test of the efficacy of the lamp, it may be lighted and suspended within a large gas-jar, to the bottom of which, a current of coal-gas is conducted by a vulcanized rubber tube. The effects produced by mixtures of coal-gas and air, in various proportions, can thus be observed. If there is a deficiency of oxygen, the lamp will be extinguished; if the quantity of gas is in very small proportion, combustion will be continued with an elongated flame. In explosive proportions, the mixture will penetrate the lamp and burn in the interior of the gauze-cylinder, temporarily extinguishing the flame. If suddenly raised into the air, the flame will sometimes be re-kindled; but in no case, if the wire-gauze is in a sound condition, will the flame be communicated to the gaseous contents of the jar.

In the use of this lamp in coal mines the cylinder should be locked or securely fastened to the lamp, and on no pretence removed while it is employed for mining purposes. The real object of this invention has been, to a great extent, defeated by ignorance and carelessness. Davy's experiments have shown that the state of the flame will always give warning of danger. The lamp is admirably adapted to test with safety the condition of the air in the shafts and galleries of coal mines, and to warn the miner of the spots where it would be unsafe to commence, or continue work, until the fire-damp had been removed by proper ventilation. As the explosive mixture is not noxious to breathe, miners continue to use the lamp long after it has indicated danger. The gauze may become red-hot by the continued combustion of the mixture within the lamp; the flame may be driven through the meshes by a strong current of the gas from *blowers*, or a small particle of coal-dust may strike upon the red-hot wire and be kindled into flame, when the whole mixture will be exploded, with a great destruction of life, arising from burning, from serious mechanical injury, or from suffocation as a result of the carbonic acid produced in the explosion. The accidents which have almost annually led to a great destruction of life in coal mines have been wrongly attributed to the use of the lamp. They have been rather due to its abuse. The removal of the gauze-cylinder—or, where locked, the perforation of it for obtaining more light—the use of tobacco and gunpowder in coal mines, are the principal causes of these accidents, when it has been possible to trace them.

The fire-damp, being very light, ascends and collects in hollows or recesses at the upper parts of the workings; so that while the lower part or floor may be ventilated and free from danger, a light brought near to the roof might lead to a dangerous explosion. For the prevention of accidents a better system of ventilation is required, and a more strict supervision of the mode in which safety-lamps are used by miners.

Explosions in houses from an accumulation of coal-gas and its admixture with air are equally formidable, and depend on similar chemical principles. There is, however, always ample warning in these cases by the powerful odor which announces the escape of coal-gas, long before it has reached its explosive proportion. Instead of opening doors and windows, and keeping at a distance all lights, until the smell has disappeared, the ordinary practice is to apply a light for the purpose of ascertaining where the leakage has occurred. The whole of the air in a room may be in an explosive state, but the coal-gas has a great tendency to accumulate at the upper part. Hence it is this part which should be thoroughly ventilated. A lighted candle may burn on the floor of a room, but, if raised a few feet above it, it may cause a violent explosion. In no case, however, can this accumulation occur without full warning being given by the odor of the gas, which is perceptible when mixed with 500 times its volume of air. (*See*, on the subject of gas-explosions in houses, a paper in the *Medical Gazette*, vol. xlii. p. 343.)

OLEFIANT GAS.—*Elayle. Carburet of Hydrogen. Bicarburetted Hydrogen* (C_2H_2).—This gas was discovered in 1796, by the Dutch chemists, who gave to it the name which it commonly bears, owing to the property which it possesses of forming an oily compound with chlorine.

It is usually obtained by the decomposition of alcohol by concentrated sulphuric acid. For this purpose, about two parts of the acid and one of alcohol (by measure) are put into a capacious retort, and heated by a lamp; when the mixture boils, the gas is evolved with sulphurous and carbonic acids; and a carbonized mass remains in the retort. It may be collected over water, and should be well washed with lime-water, or with a solution of potassa, in order to remove carbonic and sulphurous acids; it also retains a little ethereal vapor, which may be removed by agitating it with weak alcohol and afterwards with water. During the distillation, the black carbonaceous mass is apt to fill the retort and pass over into the bath. To prevent an accident of this kind, the heat should be applied around the body of the retort by a circular jet of gas, and sand or broken glass may be mixed with the liquids before the heat is applied.

The changes which take place in the production of this gas may be thus represented: Alcohol is $C_4H_6O_2$, a constitution which is equivalent to two volumes of olefiant gas $2(C_2,H_2)$ and two volumes of aqueous vapor $2(HO)$. By the action of sulphuric acid, at a temperature of about 320°, the alcohol is resolved, by a catalytic action (p. 54), into these compounds, while the water is retained by the acid in the receiver ($C_4H_6O_2+SO_3HO=2C_2H_2+SO_3,3HO$). There are other and more complicated changes in the latter stage of the distillation, as the carbon of the alcohol then decomposes part of the sulphuric acid, forming the two gaseous acid products which contaminate the gas: these changes will be considered at another time.

Properties.—Olefiant gas is colorless, and neutral in reaction. It has been liquefied by pressure, and cooling to —166°, but not solidified. Even when purified, it retains a slight ethereal odor. It acts like a narcotic poison when breathed. Water dissolves about 12·5 per cent. of its volume. It is dissolved more freely by fuming sulphuric acid, and by the ammoniacal solution of the subchloride of copper. It extinguishes all burning bodies, but is itself highly combustible, burning with a bright white flame, similar to that of burning oil, tallow, wax, or a coal-fire. It evolves much light during combustion: the particles of carbon, of which it contains a large quantity, being rendered incandescent by the combustion of the hydrogen. A portion of this carbon is deposited on any cold surface introduced into the flame. When mixed with a large proportion of air it burns with a pale flame, the carbon being then entirely consumed as well as the hydrogen. If a taper is suddenly plunged to the bottom of a jar of the gas it will kindle the gas, but be itself extinguished. If the taper is withdrawn, and a quantity of water is poured through the burning gas so as gradually to fill the jar, the gas will be brought to the surface, and burnt in a large sheet of flame. If lime-water is added to another jar, during its combustion, this liquid will be rendered milky, showing the production of carbonic acid. This may also be proved by burning the gas from a jet under a jar of air, and afterwards testing the contents of the jar with lime-water.

When mixed with three times its volume of oxygen, and the mixture is exploded, either by flame or the electric spark, it is converted, with a violent detonation, into carbonic acid and water:—

$$\underbrace{C_2H_2}_{\text{1 vol.}} + \underbrace{O_6}_{\text{3 vols.}} \text{ (15 vols. air)} = \underbrace{2CO_2}_{\text{2 vols.}} + \underbrace{2HO}_{\text{2 vols.}}$$

Its composition may be deduced from these results:—the 2 vols. of carbonic acid represent 2 vols. or equivalents of carbon, with 2 vols. of oxygen; while 2 vols. of aqueous vapor represent 2 vols. of hydrogen, and 1 vol. of oxygen:—

	Atoms.	Weights.	Per cent.	Vols.	Sp. Gr.
Carbon . . .	2	12	85·7	2	0·8292
Hydrogen . .	2	2	14·3	2	0·1382
	1	14	100·0	1	0·9674

The specific gravity of olefiant gas is therefore about 0·9674, and, compared with hydrogen, it is 14 to 1. 100 cubic inches weigh 29·96 grains. Its refractive power is 1·818, air being =1·000:—its specific heat, compared with that of air, is 1·53 (DULONG), being greater than that of any other gas. As it is usually prepared, it is often associated with other hydrocarbon vapors, which may affect its physical properties. A mixture of this gas with oxygen is converted into acetic acid by spongy platinum, and its solution in sulphuric acid has, by agitation in water and mercury, produced alcohol. (BERTHELOT). When passed through a tube heated to redness, it deposits one-half of its carbon, and is changed into light carburetted hydrogen. If, however, the tube is heated to whiteness, all the carbon is deposited, and each volume of the gas yields two volumes of hydrogen.

The action of chlorine on olefiant gas is remarkable. When the gas is mixed with chlorine, in the proportion of 1 to 2 by volume, the mixture, when inflamed, produces, without explosion, hydrochloric acid, and black amorphous carbon is abundantly deposited. If the gases be well mixed, and then inflamed in a tall and narrow glass jar (about 2 feet high and 4 inches in diameter), placed with its mouth upwards, the experiment is very striking; a deep-red flame gradually descends through the mixture, and a dense black cloud of carbon rises into the atmosphere; fumes of hydrochloric acid are at the same time formed, and a peculiar aromatic odor is evolved

($C_2H_2+2Cl=2HCl+2C$). The hydrochloric acid may be detected by its effect on litmus-paper, and the production of white fumes with ammonia.

CHLORIDE OF OLEFIANT GAS (C_2H_2Cl); *Dutch Liquid; Chloric Ether.*—If chlorine and olefiant gases be merely mixed, in equal volumes, over water, or in a clean and dry glass globe, exhausted of air, they act slowly upon each other, and a peculiar liquid is formed, which appears like a heavy yellow oil; hence the term *olefiant gas*, applied to this hydrocarbon by the Dutch chemists, and *Elayle* (from ἔλαιον, and ὕλη, *the source of an oil*) by Berzelius. It may also be formed by allowing a current of each gas to meet in a proper receiver; but there should always be an excess of olefiant gas, for if the chlorine is in excess, the liquid will absorb it. To purify it, it should be washed in water, and then carefully distilled over fused chloride of calcium.

This compound is a transparent and colorless liquid; its taste is sweet, and somewhat acrid; its odor fragrant. Its specific gravity is 1·2. It boils at 180°. According to Gay-Lussac, the specific gravity of its vapor is 3·45. It burns with a green flame, evolving hydrochloric acid, and depositing carbon. It is decomposed when passed through a red-hot tube. It has been employed as an anæsthetic, but has been found too stimulating. Olefiant gas forms a similar compound with the vapor of bromine.

Oil Gas (C_4H_4).—This is a gaseous compound, containing in each volume, as its vapor density proves, double the proportions of carbon and hydrogen existing in olefiant gas. It was obtained by Faraday as one of the products of the destructive distillation of oil. He called it bicarburetted hydrogen. As a gas, it has a sp. gr. of 1·9264; it burns with a brilliant, white, smoky flame. It is not dissolved by water, but is soluble in alcohol and the oils. When cooled to zero, it is condensed into a colorless, light liquid, having a sp. gr. of 0·627.

CARBON AND NITROGEN.—These elements form three different compounds; a gaseous body, cyanogen, NC_2; and two solids, paracyanogen, N_2C_4, and mellone, N_4C_6.

CYANOGEN (NC_2, or $Cy=26$). *Bicarburet of Nitrogen.*—This gaseous compound was discovered, in 1815, by Gay-Lussac, and termed *cyanogen* (from κύανος, *blue*, and γεννάω, to *generate*), in consequence of its being essential to the production of Prussian blue. It is sometimes formed by the direct action of nitrogen upon carbon in the presence of bases, as where nitrogen or air is passed over a mixture of charcoal and carbonate of potassa, heated to redness. Under these circumstances, cyanogen is produced, and enters into combination with the metal potassium ($KO,CO_2+C_4+N=K,NC_2+3CO$). Cyanide of potassium is thus sometimes produced and deposited in the crevices of the walls of blast-furnaces. When an organic substance containing nitrogen and carbon is heated, these elements will not unite directly; but if heated with the alkaline metals, potassium or sodium, in a glass-tube, out of contact of air, they instantly combine to form cyanogen, and this body unites with the metal, to produce a metallic cyanide. This conversion has already been described as one of the best methods of detecting nitrogen in organic matter (p. 143). In the destructive distillation of coal, the nitrogen and carbon combine to form cyanogen, which is found in the solid products in combination with ammonia and lime. Sulphocyanogen is also produced under these circumstances, as the cyanogen combines with a portion of the sulphur of coal.

Preparation.—Cyanogen may be obtained in the gaseous state by heating well-dried cyanide of mercury in a small retort to dull redness. The gas readily comes over, and, as it is dissolved by water, it should be collected and preserved over mercury. Although cyanogen and mercury are both volatile bodies, it is impossible to obtain more than one-third of the cyanogen present in the cyanide [$3HgCy=NC_2$ (cyanogen) $+N_4C_4$ (paracyanogen) $+3Hg$]. Mercury sublimes, but there remains in the retort a brownish-black, spongy-looking solid, which from its composition has been called *paracyanogen.* It is equivalent to two atoms of cyanogen, and is polymeric with it ($2NC_2=N_2C_4$). When strongly heated in air, this residue yields carbonic acid, and leaves CN; but it is very difficult of combustion. Cyanogen is so easily decomposed by the elements of water, that great care should be taken to dry the cyanide of mercury thoroughly before it is submitted to heat; and no moisture should be present in the jars in which the gas is collected.

Properties.—Cyanogen is a colorless neutral gas, of a pungent odor, irritating to the eyes, and highly poisonous if breathed even in a diluted state. Its specific gravity when compared with hydrogen is as 26 to 1; and with common air, as 1·796 to 1; 100 cubic inches weigh 55·64 grains. It sustains a high temperature in porcelain tubes without decomposition. Under a pressure of between three and four atmospheres at the temperature of 45°, Faraday condensed cyanogen into a limpid colorless liquid, of a specific gravity of about 0·9, and a refractive power rather less than that of water. When a tube containing it was opened, the expansion within appeared inconsiderable, and the liquid slowly evaporated, producing intense cold. It does not conduct electricity. At temperatures below —30°, it becomes a transparent crystalline solid.

It extinguishes a lighted taper, but takes fire and burns with an inner rose-red flame, surrounded by a blue flame. Carbonic acid and nitrogen are the sole products of this combustion. Four equivalents or two volumes of oxygen are required for its entire combustion ($NC_2+O_4=2CO_2+N$). In these proportions the mixture is explosive by heat or electricity. A red-hot platinum wire, or the electric spark, will kindle the gases instantly. The production of carbonic acid as a result of its combustion, may be proved by burning the gas from a jet under a jar of air, and subsequently adding lime-water to the contents of the jar. All ordinary combustibles are extinguished in it. Alkaline metals may, however, be burnt in it as readily as in chlorine. Potassium or sodium heated to ignition and introduced into the gas, undergoes vivid combustion, and the cyanogen combines directly with the metal to form a metallic cyanide. It is this property of entering into combination like an element, and the fact that with hydrogen it forms a hydracid in every respect analogous to those produced by the halogens, which have induced chemists to designate cyanogen as a *compound radical,* and to associate it with chlorine, bromine, and iodine. Its existence shows that a body may have all the ordinary chemical properties assigned to an element, and yet be of a compound nature.

Cyanogen does not bleach organic colors. Water will dissolve 4·5 volumes of the gas; alcohol will dissolve 23 volumes; and it is also taken up by ether and oil of turpentine. Its aqueous solution is rapidly decomposed by exposure to light; it acquires at first acid and afterwards alkaline properties, cyanic acid and ammonia being products of this reaction. Oxalate and carbonate of ammonia, formate of ammonia, urea, and paracyanogen, are also products, in different stages of decomposition, of the aqueous solution. Iodine, sulphur, and phosphorus may be sublimed in the gas without change. Dry chlorine has no action on dry cyanogen; but when moist and exposed to light, a yellow oil is produced, which appears to be a mixture of chloride of carbon and chloride of nitrogen (SERULLAS), furnishing another proof of the importance of water to bring about chemical changes in bodies (*see* pages 41 and 130).

The gas is readily dissolved by alkaline liquids; and, as with the halogens, a cyanate of the alkali and cyanide of the metal are produced. Oxide of mercury in a humid state, also absorbs the gas, forming a soluble cyanide.

Composition.—Cyanogen may be passed through a porcelain tube intensely heated without undergoing any change; but if passed through a red-hot iron tube, carbon is deposited, and a volume of nitrogen, equivalent to the cyanogen employed, is set free. If one volume of this gas is mixed with two volumes of oxygen, and the mixture is detonated by the electric spark over mercury, two volumes of carbonic acid and one volume of nitrogen result; hence, deducting the oxygen employed, each volume of this gas must consist of two volumes of carbon vapor, and one volume of nitrogen condensed into a single volume of the gas.

	Atoms.	Weights.	Per. cent.	Vols.	Sp. Gr.
Nitrogen	1	14	53·85	1	0·9674
Carbon	2	12	46·15	2	0·8292
	1	26	100·00	1	1·7966

Test.—The colored flame of the gas during combustion, and an examination of the products, carbonic acid and nitrogen, are sufficient to identify it.

Compounds.—Cyanogen combines directly with metals, like an element, forming cyanides of metals analogous to oxides and chlorides; it forms acids with oxygen and hydrogen, and compound radicals with sulphur and iron, which also combine with hydrogen to form acids, and with metals to form peculiar classes of salts. The metallic cyanides are remarkable for the readiness with which they produce double salts. The subjoined list comprises the principal derivative compounds of cyanogen:—

Cyanogen	Cy	Cyanide	MCy
Cyanic acid	Cy, O	Cyanate	MO,CyO
Fulminic acid	Cy_2,O_2	Fulminate	Cy_2O_2, 2MO
Cyanuric acid	Cy_3,O_3	Cyanurates	Cy_3O_3, 3MO
Hydrocyanic acid	HCy + MO =	Cyanide	MCy, (HO)
Sulphocyanogen	S_2Cy	H Hydrosulphocyanic acid M Sulphocyanide	
Ferrocyanogen	$FeCy_3$	H_2 Hydroferrocyanic acid M_3 Ferrocyanide	
Ferricyanogen	Fe_2Cy_6	H_3 Hydroferricyanic acid M_3 Ferricyanide	
Nitroferricyanogen	$Fe_2Cy_5NO_2$	H_2 Nitrohydrocyanic acid M_2 Nitroprusside	

MELLONE (N_4C_6).—The third compound of carbon and nitrogen is a solid substance of a yellow color, produced in the destructive distillation of sulphocyanogen. It may be heated to dull redness without change, but at a higher temperature it is resolved into three volumes of cyanogen and one of nitrogen ($N_4C_6=3NC_2+N$). It is a compound radical, and combines directly with metals to form *Mellonides.* According to Gerhardt, it always contains hydrogen.

CYANOGEN AND OXYGEN.—These bodies form three homologous acids, the cyanic (CyO), the fulminic (Cy_2O_2), and the cyanuric (Cy_3O_3). They are monobasic, bibasic, and tribasic, respectively.

CYANIC ACID (CyO).—When cyanogen is passed into an alkaline solution, a cyanide and a cyanate are formed ($2BaO+2Cy=BaCy+BaO,CyO$), and so far the action of cyanogen corresponds to that of chlorine: but the extreme tendency of the cyanates' so formed, to decomposition, prevents their separation. A permanent cyanate may be obtained by the following process: six parts of ferrocyanide of potassium and two of carbonate of potassa, both carefully dried (anhydrous), are intimately mixed in fine powder with eight parts of pure and dry peroxide of manganese: this mixture is heated for some time to dull redness, until a portion cooled and dissolved in water, does not give a blue precipitate with a persalt of iron. The contents of the crucible are then allowed to cool, reduced to powder, and boiled for fifteen minutes in alcohol, sp. gr. ·850. The liquid is filtered hot, and on cooling, it deposits crystals of cyanate of potassa. The alcohol is poured from the salt and again boiled with the residue, so long as further portions of cyanate can be thus obtained. The salt should be well dried by pressure in filtering paper, and afterwards *in vacuo* over sulphuric acid; it must be preserved out of contact of air and moisture, otherwise it will soon pass into ammonia and carbonate of potassa. Although the cyanic acid may thus be obtained in union with a base, any attempt to set it free by means of another acid, is attended by its immediate decomposition into carbonic acid and ammonia. Wöhler endeavored to procure the acid in a pure state, by decomposing cyanate of silver by dry hydrochloric acid. The product, however, was hydrated cyanic acid with one equivalent of hydrochloric acid gas; hence, when brought into contact with water, it was immediately resolved into hydrochlorate of ammonia and carbonic acid. Cyanic acid, in the presence of water, cannot be separated from its salts without undergoing immediate decomposition. Liebig found that it might be procured in a concentrated form as hydrate, by heating cyanuric acid in an air-tight retort, connected with a receiver surrounded by ice. These acids contain the same elements, and are mutually convertible the one into the other; but cyanic acid is a simple atom, while cyanuric acid is a complex atom.

Properties.—This acid in its concentrated state (HO,CyO) is a limpid colorless liquid. It is intensely corrosive and strongly acid. Its vapor is very pungent, like that of the strongest acetic acid, and it is very irritating to the eyes and nose; but it is not inflammable. When diluted with a little water and retained at 32°, its odor is like that of acetic acid, but it soon begins to change: carbonic acid is evolved, carbonate and cyanate of ammonia are formed, and, by evaporation, crystals of urea may be obtained. In this case one atom of cyanic acid and three of water, at first yield one atom of bicarbonate of ammonia; $C_2N,O+3HO=NH_3,2CO_2$: but the cyanic, being a stronger acid than the carbonic, the undecomposed cyanic acid combines with the ammonia and expels carbonic acid; and, on evaporation, the cyanate of ammonia combines with an atom of water to form urea; $NH_3,HO,C_2NO=C_2H_4O_2N_2$.

Hydrated cyanic acid, as obtained by the method above described, when it has cooled to 60°, becomes turbid and milky-looking; it acquires heat spontaneously, begins to boil, and then passes into a pasty-looking solid, while there are sudden evolutions of gas with explosions, from the unchanged portion of the acid. It is ultimately converted into a dry, solid, uncrystalline white substance, which is called *Cyamelide* (Liebig). These remarkable changes take place rapidly at the common temperature, and quite independently of air and moisture. They also take place at the freezing-point, but more slowly, and no gas is evolved under these circumstances.

Cyamelide is insoluble in water, nitric acid, and hydrochloric acid, either separately or mixed as aqua regia. It is dissolved by potassa with evolution of ammonia, and cyanurate of potassa is obtained by evaporation. Concentrated sulphuric acid dissolves it when the mixture is moderately heated, with escape of carbonic acid and the production of sulphate of ammonia. The products of its decomposition are therefore the same as those of cyanic acid in water, and when cyamelide is distilled by itself it is reconverted into hydrated cyanic acid. It is therefore an isomeric solid condition of this acid.

Cyanates.—The cyanates of the alkalies alone are soluble in water, and are not decomposed by a red heat. When an aqueous solution of an alkaline cyanate is heated, carbonic acid and ammonia are produced ($NC_2O+3HO=NH_3+2CO_2$). The nitrates of lead, silver, and mercury give with the solution of a cyanate white precipitates. When mixed with sulphate of ammonia, and evaporated to dryness, a solution of a cyanate yields urea. When hydrated cyanate of ammonia is gently heated either in the dry state or in solution, it is converted into urea (Wöhler). These substances are metameric (*see* page 18). When an acid is added to a cyanate, either solid or in solution, there is effervescence, owing to the production and escape of carbonic acid. The strong pungent odor of hydrated cyanic acid will be perceptible, and a salt of ammonia is formed in the liquid. Hence a cyanate cannot be mistaken for a carbonate.

FULMINIC ACID $2(C_2N)O_2$ or (Cy_2O_2).—Under the articles MERCURY and SILVER, the process for preparing detonating compounds of these metals, by acting upon their nitric solutions by alcohol, will be described. The oxides are united to an acid containing the same elements, and in the same relative proportions, as the cyanic acid, to which, in that particular state of combination, the term *Fulminic Acid* has been applied; but the equivalent of the fulminic acid is exactly double that of the cyanic. This acid has not been isolated: it is known only in combination with bases.

Fulminic acid, therefore, cannot be obtained as such from the bases with which it is combined; at the moment of its separation by a stronger acid, it is resolved into hydrocyanic acid and other products. Hence we have in this compound an acid in which the metal cannot be replaced by hydrogen (*see* page 69).

Fulminates.—These are bibasic salts containing either two atoms of fixed base (neutral fulminates), or one atom of fixed base and one atom of water. The two atoms of fixed base may be represented by two atoms of the oxide of an easily reducible metal, or by two atoms of the oxides of two different metals, also easily reducible. There are no fulminates of two alkaline bases. The fulminates explode by concussion, friction, heat, or contact with concentrated sulphuric acid. They evolve hydrocyanic acid when treated with hydrochloric acid.

CYANURIC ACID ($C_6N_3O_3$ or Cy_3O_3).—This acid may be obtained in combination with three atoms of water, as $3HO+Cy_3O_3$. Scheele first described it under the name of pyro-uric acid. He procured it by the destructive distillation of uric acid. It exists in the hydrated and anhydrous states. It is dissolved by strong sulphuric or nitric acid without change, and is precipitated by water. The alkaline *cyanurates* evolve, when heated, hydrated cyanic acid, cyanate of ammonia, carbonic acid, and nitrogen, leaving a residue of cyanate.

The cyanic, fulminic, and cyanuric acids, although composed of similar proportions of the same elements, are widely different in properties—a fact which appears to show that, in compounds of a quasi-organic character, the properties of bodies are more dependent on molecular arrangement than on atomic constitution. The cyanuric acid alone can exist in the anhydrous state, and remain unchanged in contact with water and other acids. This acid alone is soluble in alkalies without change, and may be separated from its alkaline solution by acids in an unaltered state. Cyanurate of silver will bear a temperature of 300°, without undergoing decomposition. At this temperature, cyanate of silver is decomposed with ignition and evolution of carbonic acid and nitrogen (LIEBIG), while fulminate of silver under the same circumstances is decomposed with detonation, a double amount of carbonic acid and nitrogen being produced. Although fulminic acid is the intermediate compound, it cannot be procured either by the intermixture of the cyanic and cyanuric acids, or by the action of any chemical reagents upon them. In this respect these three compounds somewhat resemble the hydrates of phosphoric acid, the first being converted at once into the third, without the production of the second hydrate (p. 226). In phosphoric acid, the difference arises from an increase in the atoms of water of hydration: in these acid compounds of cyanogen, the first and last members of the series only are hydrated; and there is an increase in the proportion of the elements as well as of the atoms of water. In reference to fulminic acid, it is worthy of note that, as in an isolated state, it will not combine with the elements of water, its existence proves, among other facts, that acids are not necessarily salts of hydrogen (*see* p. 85).

CYANOGEN AND HYDROGEN. HYDROCYANIC ACID.—*Cyanhydric Acid. Prussic Acid.* (C_2N,H, or HCy).—This compound was first obtained by Scheele in 1782. It was not, however, until the discovery of cyanogen by Gay-Lussac, in 1815, that its real nature was understood, and its components accurately determined. Cyanogen and hydrogen have no tendency to direct combination, but by the action of certain acids on metallic cyanides, hydrocyanic acid is produced by double decomposition: in this way it is obtained by the action of hydrochloric acid on dry cyanide of mercury or silver ($AgCy+HCl=AgCl+HCy$). The mixture may be distilled in a sand-bath, and the product collected in a receiver kept cool by a freezing mixture. In order to obtain anhydrous hydrocyanic acid, the following process is preferable. Introduce the dry cyanide of mercury into a long glass tube, terminating at one extremity in a receiver immersed in a freezing mixture, and then, from a proper apparatus, pass over it a stream of pure and well dried sulphuretted hydrogen, the sulphur of which combines with the mercury to form sulphide of mercury, while the hydrogen unites to the cyanogen to form hydrocyanic acid ($HgCy+HS=HgS+HCy$). The vapor of the acid may be driven, by the application of a gentle heat, into the cold receiver, and there condensed. The ordinary process for obtaining this acid, consists in distilling by a gentle heat 10 parts of finely powdered ferrocyanide of potassium, with a mixture of 5 parts of sulphuric acid and 14 of water: the product should be collected in a well cooled receiver. The acid may be concentrated by digesting it with chloride of calcium. Any Prussian blue may be separated from it by re-distillation. The hydrocyanic acid thus procured, should be preserved in a well-stopped phial. In this process, the cyanide of potassium of the ferrocyanide, is decomposed by the hydrated sulphuric acid. $KCy+HO,SO_3=KO,SO_3+HCy$. Cyanide of potassium may be substituted for the ferrocyanide. Hydrocyanic acid forms no definite hydrate with water: hence, according to Millon, it may be obtained anhydrous from the most diluted solution with as little trouble as absolute alcohol. He submits the diluted acid to fractional distillation, collecting the distillate between 120° and 212°. After two or three distillations, he passes the vapor through two Woulfe's bottles, containing dry chloride of calcium, and condenses it in a receiver, placed in a freezing mixture. The heat of distillation in the last stage is not allowed to exceed 176°.

Properties.—Anhydrous hydrocyanic acid is a colorless liquid: its vapor when diffused in air, has an odor resembling that of bitter almonds. Its taste, when diluted with water, is warm and acrid, and it is highly poisonous, so that the utmost care should be taken to avoid the inhalation of its vapor. The respiration of a small quantity of this vapor, even in a diluted state, produces an acrid sensation in the nose and throat, dizziness, sense of weight in the head, and insensibility. It is irritating to the eyes. The vapor readily traverses by osmosis, paper, animal membrane, and even caoutchouc. The anhydrous acid is the most powerful poison known, whether we regard the smallness of the dose or the rapidity of its operation. Less than a grain of the acid has destroyed the life of an adult in twenty minutes. The anhydrous acid volatilizes so rapidly as to freeze itself, when a drop of it is placed on a glass-plate. Its specific gravity at 64° is 0·696: and the specific gravity of its vapor, as experimentally determined by Gay-Lussac, is 0.9476; it boils at 80°, and congeals at 3°, or 4° above 0° in its ordinary state; but when it is perfectly anhydrous, it remains liquid according to Schultz at —40°. It burns with a bright flame. It scarcely affects the blue of litmus. It is very liable to spontaneous decomposition, especially under the influence of light, becoming brown, evolving ammonia, and depositing paracyanogen, changes which are prevented by the presence of minute portions of other acids, but are accelerated by traces of ammonia or other bases. The pure anhydrous acid is decomposed spontaneously, whether kept in the light or dark, whether in open or closed vessels. If highly concentrated, it solidifies into a brownish-black jelly-like mass. When mixed with strong hydrochloric acid, it soon solidifies into a pure crystalline mass of hydrochlorate of ammonia. Millon found that the anhydrous acid forms other compounds, which are only stable, so long as water is excluded. Moisture destroys them, and formate of ammonia is produced. The effect of ammonia upon this liquid is remarkable: a few bubbles of the gas were found to solidify several ounces of the anhydrous acid. Dilution with water delayed, but did not prevent this result. The preservative effects of acids, appear to depend on the neutralization of ammonia or the prevention of its production. When water is present, the concentrated inorganic acids resolve it into ammonia and formic acid: 3 atoms of water and 1 of hydrocyanic acid include the elements of 1 atom of formate of ammonia; $3HO + C_2,N,H = C_2,H,O_3 + NH_3$. It is resolved by dry chlorine, under the influence of the sun's rays, into hydrochloric acid and chloride of cyanogen. The changes produced by acids in the constitution of hydrocyanic acid, show that an excess of hydrochloric or sulphuric acid employed in its preparation may lead to its decomposition and contamination with formic acid. As a singular fact connected with this conversion, Liebig has noticed that when formate of ammonia is transmitted through a glass tube, heated to dull redness, it is decomposed and is reconverted into hydrocyanic acid and water.

$$\begin{array}{ccccl} C_2H & + & N & = & \text{1 atom of hydrocyanic acid.} \\ O_3 & + & H_3 & = & \text{3 atoms of water.} \\ \cline{1-1}\cline{3-3} \text{1 atom of formic acid.} & & \text{1 atom of ammonia.} & & \end{array}$$

The easily reducible oxides (of mercury and silver) decompose hydrocyanic acid, and yield water and a metallic cyanide. When lime or baryta is heated to redness in hydrocyanic acid vapor, they afford cyanides and cyanates, and hydrogen is evolved.

In the voltaic circuit, hydrocyanic acid yields hydrogen at the negative, and cyanogen at the positive electrode, but the aqueous solution of this acid, when pure, is a very bad conductor of electricity. When its vapor is mixed with oxygen it may be exploded by the electric spark, in which case 2 volumes of hydrocyanic acid vapor require for perfect combustion 2 volumes and a half of oxygen: the results are water, 2 volumes of carbonic acid, and 1 volume of nitrogen $(H,NC_2 + O_5 = 2CO_2 + HO + N)$. When potassium is heated in its vapor, cyanide of potassium is formed, and hydrogen, equal to half the volume of the acid is liberated: it appears, therefore, that there is the strictest analogy between the hydrocyanic and the other hydracids, and that 1 volume of cyanogen and 1 of hydrogen form 2 volumes of the vapor of hydrocyanic acid. In contains in each volume, half a volume of hydrogen and half a volume of cyanogen.

	Atoms.	Weights.	Per cent.	Vols.	Sp. Gr.
Hydrogen	1	1	3·70	1	0·0691
Cyanogen	1	26	96·30	1	1·7966
	1	27	100·00	2	1·8657

And 1·8657÷2=0·9328, the sp. gr. of hydrocyanic acid vapor. The experimental result of Gay-Lussac, makes it rather higher. 100 cubic inches of the vapor weigh 28·89 grains; compared with hydrogen, hydrocyanic acid vapor has a sp. gr. of 13·5. The anhydrous acid is miscible in all proportions with water, alcohol, and ether.

This acid forms no definite *hydrate* but in various states of dilution, it is used in medicines as a sedative, and certain processes are recommended for at once obtaining it of a convenient strength for pharmaceutical purposes. The Pharmacopœial hydrocyanic acid contains 2 per cent. of anhydrous acid, while that which is sold under the name of *Scheele's* acid, contains from 4 to 5 per cent. A dose of Scheele's acid exceeding 20 drops, and an equivalent portion of any of the other solutions of the acid, would generally suffice to destroy life. Diluted hydrocyanic acid of the sp. gr. 0·982 at 54°, contains 10·53 per cent. of anhydrous acid (TRAUTWEIN). The process for preparing diluted hydrocyanic acid for officinal purposes, consists in the decomposition of ferrocyanide of potassium (FeCy,2KCy), by diluted sulphuric acid. The proportions are somewhat different from those above described,but the process is similar.

Liebig recommends for obtaining diluted hydrocyanic acid, the distillation of a mixture of equal parts of cyanide of potassium and sulphuric acid; the cyanide being dissolved in twice its weight of water, and the acid diluted with three times its weight of water: these solutions are to be gradually mixed, and the mixture cautiously distilled. This acid is a product of the distillation of the bitter almond, the kernels of the peach, nectarine, and other seeds of the like nature. It may also be procured by distilling the young shoots of laurel.

As pure hydrocyanic acid, even in a diluted state, is still liable to decomposition, it should be prepared in small quantities, and preserved in well-stopped phials out of the presence of light: or a very minute addition of diluted sulphuric or hydrochloric acid may be made to it, by which its tendency to change is prevented.

When diluted hydrocyanic acid is pure, it leaves no residue on evaporation, and only slightly and transiently reddens litmus: if it contain any of the stronger acids, its action on vegetable blues is very decided. Under these circumstances, also, it throws down red iodide of mercury from the solution of the double salt of iodide of potassium and cyanide of mercury; but in using this test no alcohol must be present, as it would retain the cyanide of mercury in solution. (GEOGHEGAN, *Ph. Mag. and Journ.* vii. 400.)

Officinal hydrocyanic acid may contain as impurity, hydrochloric or sulphuric acid, and occasionally Prussian blue. The latter substance is deposited on standing, or readily separated by careful distillation. In order to detect hydrochloric acid, ammonia is added, and the liquid is concentrated by evaporation. The hydrocyanate of ammonia is volatilized, while the hydrochlorate of ammonia remains in prismatic crystals. A solution of these crystals may be tested by the addition of nitrate of silver. The chloride of silver, with its characteristic property of insolubility in nitric acid, is thrown down. A solution of borax, free from chloride of sodium, may be employed instead of ammonia. This fixes the hydrochloric acid alone. Sulphuric acid may be detected by the addition of nitrate of baryta; if present, a white precipitate of sulphate of baryta, insoluble in nitric acid, is deposited.

Hydrocyanic acid is a weak acid: it will not decompose the alkaline carbonates, or set free carbonic acid from these salts; but it separates silicic acid from the soluble alkaline silicates. It dissolves the oxide of mercury, and this solution is not precipitated by alkalies ($HgO+HCy=HgCy+HO$). It decomposes a solution of subnitrate of mercury, giving a gray precipitate of the reduced metal ($HCy+Hg_2O=HgCy+Hg+HO$). It has no action on solutions of the chloride and nitrate of mercury. Among other chemical properties, it gives a white cyanide, insoluble in cold nitric acid, with a solution of nitrate of silver ($AgO,NO_5+H,Cy=AgCy+HO,NO_5$). Unless it contains sulphuric acid, it does not precipitate a salt of baryta. It does not affect a persalt of iron, and produce with it no Prussian blue when an alkali is added to precipitate the oxide. It does not precipitate a solution of the green sulphate of iron, but produces Prussian blue on the addition of an alkali, by a reaction of its elements on the mixed oxides of iron which are precipitated. This may be proved by adding diluted hydrochloric acid to the mixture: the oxide of iron is dissolved, and Prussian blue remains. It does not affect a solution of copper until potassa is added, when white subcyanide of copper, insoluble in hydrochloric acid, is produced. When the sulphate of copper is previously mixed with a small quantity of sulphurous acid, the white subcyanide of copper (Cu_2Cy) is formed, and slowly deposited. Hydrocyanic acid destroys the color of iodine in aqueous solution, as well as the blue color of iodide of starch.

However carefully diluted hydrocyanic acid may have been prepared, its real strength should always be determined by experiment, for the specific gravity is no adequate criterion. Neither the proportions of materials used, nor the specific gravity of the product, can convey any accurate knowledge of the strength of the acid. The strength of the medicinal acid may be obtained by precipitating a given weight of it by nitrate of silver, which throws down an insoluble cyanide of silver, of which 134 parts are equivalent to 27 of anhydrous hydrocyanic acid; so that if the weight of the precipitated cyanide of silver (well washed, and carefully and perfectly dried,) be divided by 5, or multiplied by 0·2015 ($27 \div 134$) the product will almost exactly represent the quantity of real acid. One hundred grains of officinal acid, of a strength of 2 per cent. should therefore give 10 grains of dry cyanide of silver; and 100 grains of Scheele's acid should give from 20 to 25 grains of dry cyanide. From the result of such an analysis it is easy, by the addition of water, to reduce a strong acid to any assignable strength.

Tests for Hydrocyanic Acid. Analysis in cases of Poisoning.—The peculiar odor of the acid is perceptible in liquids, unless other strong odors are present. 1. *Nitrate of Silver.* This throws down a heavy white precipitate (cyanide of silver) unchanged by exposure to light. It is insoluble in cold nitric acid. When well dried and heated in a small reduction-tube it melts, and evolves a gas which burns with the rose-red and blue colored flame of cyanogen.—2. *Sulphate of Iron.* Add to the liquid a few drops of a solution of green vitriol, followed by a solution of potassa, and agitate the mixture. It will acquire a dark bluish-green color. Add diluted hydrochloric acid; oxide of iron will be dissolved, and Prussian blue (having a greenish tint if much iron is present) will be left. Prussian blue is known by its color and insolubility in diluted acids. This test will reveal the presence of prussic acid even when mixed with alkaline chlorides and other salts.—3. *Sulphide of Ammonium.* Add to the liquid a few drops of yellow or bisulphide of ammonium, and evaporate to dryness on a sand-bath. The hydrocyanic acid is converted into sulphocyanide of ammonium ($NH_4S_2+HCy+O(air)=NH_4S_2Cy+HO$). And this is at once proved by the deep red color imparted to the residue by the addition of a persalt of iron. (*London Medical Gazette*, vol. xxxix. p. 765.)

These tests may be applied to detect the *vapor* of hydrocyanic acid, as it escapes from any simple or complex liquid which contains it. The suspected liquid is placed in a small jar, or beaker, the top of which admits of being covered by a watch-glass. A drop of nitrate of silver in the hollow of the glass, when inverted over a liquid containing prussic acid, will be whitened, owing to the production of cyanide of silver: if slowly formed, the deposit will be found under the microscope to consist of well-defined oblique rhombic prisms. A drop of a solution of bisulphide of ammonium may be added to the deposited cyanide of silver, and the mixture warmed. Persulphate of iron will produce a red color in the liquid notwithstanding the presence of black sulphide of silver. This will prove the presence of cyanogen, if the cyanide is in too small a quantity to yield evidence by combustion. In employing the iron-test for the detection of the vapor, a solution of potassa should be placed in the watch-glass, and, after sufficient exposure of the alkali to the vapor, the sulphate of iron, followed by diluted hydrochloric acid, should be added to the alkaline liquid. These tests will fail if the liquid contains sulphuretted hydrogen; but in this case, the sulphur-test will be available. The bisulphide of ammonium, placed in a watch-glass absorbs the vapor completely, and, on evaporation to dryness, the residue will be found to contain sulphocyanide of ammonium by the iron-test. These *vapor-tests* may be thus readily applied to the detection of the poison in food, in the contents or coats of the stomach or intestines, in blood, and in the substance of the heart and liver.

In order to obtain the acid from the coats of the stomach, or its contents, in cases of poisoning, the substance, cut into small pieces, should be mixed with cold distilled water, and distilled by a water-bath at a low temperature (170°), the distillate being collected in a cooled receiver. If the liquid suspected to contain the poison is alkaline, a small quantity of tartaric acid may be added to neutralize it. The colorless distillate in the receiver may then be examined for its odor, and tested by the action of the three tests above described. If the liquid of the stomach is acid, it should be neutralized; as, if ferrocyanide of potassium was present, any excess of acid would produce hydrocyanic acid from this salt. In the dead body, hydrocyanic acid is converted by putrefaction into sulphocyanide of ammonium, which may be dissolved out by alcohol, and tested. (*See Sulphocyanides.*)

Cyanides.—The salts formed by hydrocyanic acid are similar to those of the halogens. Thus, in contact with diluted alkaline solutions, water and a cyanide are produced ($KO+HCy=HO+KCy$). If the alkaline solution is concentrated, then as with the concentrated acid in the presence of water, hydrocyanic acid is resolved into formic acid and ammonia (*see* page 266). The cyanides of the alkaline and alkaline earthy metals are very soluble, producing strongly alkaline solutions, which evolve an odor of hydrocyanic acid from the action of the carbonic acid of the air. They are powerful poisons. They are readily distinguished from other salts by the fact that the weakest acid decomposes them, and sets hydrocyanic acid at liberty. This may be detected by the vapor-tests (*see* p. 268). The metallic cyanides, excepting that of mercury, are insoluble in water, and are not readily decomposed by oxacids. Hydrochloric and hydrosulphuric acids decompose them, and liberate hydrocyanic acid. Many of the metallic cyanides are soluble in, and form double salts with, cyanide of potassium. Nitrate of silver throws down from solutions of the cyanides, white cyanide of silver, possessing the characters above described. A solution of green sulphate of iron followed by a diluted acid, produces with a soluble cyanide, Prussian blue. When heated to redness, out of contact of air, the cyanides of potassium and sodium undergo no change, but if heated with exposure to air, or in contact with substances containing oxygen, cyanates of the alkalies are produced. They are powerful deoxidizers. Cyanide of potassium, owing to its fusibility, and its deoxidizing action, has been usefully employed in the arts for the soldering of metals. It removes every particle of oxide, and produces a clean surface for the solder.

CYANOGEN AND CHLORINE.—These bodies unite to form gaseous, liquid and solid compounds, which are isomeric. The *gaseous* compound (Cy,Cl) may be obtained by placing a small quantity of powdered cyanide of mercury, moistened with water, in a vessel of chlorine, taking care that it is kept in the dark. In a few days the chlorine will be replaced by the gaseous chloride. On cooling the vessel to zero, the chloride is deposited in crystals, which are soluble in water. (SERULLAS.)

The odor of this gas is pungent and irritating. It does not redden litmus, or precipitate a solution of nitrate of silver. (PELOUZE.) After some time it is spontaneously decomposed into carbonic acid and hydrochlorate of ammonia. This gas is composed of a volume of each of its constituents, which unite without condensation. The specific gravity is 2·1244, which nearly corresponds to the sum of the specific gravities of chlorine and cyanogen, $2{\cdot}4876+1{\cdot}7966\div2=2{\cdot}1421$.

Liquid Chloride (Cy_2Cl_2).—This is obtained from the same substances as the previous compound; but in this case the vessel must be exposed to sunlight. This chloride is a heavy, yellow, oily-looking liquid, insoluble in water, but soluble in alcohol.

Solid Chloride (Cy_3Cl_3).—This is a white solid crystalline substance at common temperatures. It is not very soluble in cold water, and is decomposed by boiling water into hydrochloric and cyanuric acids. It may be procured by adding a small quantity of hydrocyanic acid to a vessel of dry chlorine, and exposing it to the solar rays. These compounds are deadly poisons.

Bromide of Cyanogen (CyBr) is a colorless solid of a pungent odor, obtained by the reaction of bromine on cyanide of mercury.

Iodide of Cyanogen (CyI) is a volatile solid resembling the bromide. It is obtained by the action of iodine on the cyanide of mercury. Both are poisonous.

CYANOGEN AND SULPHUR. SULPHOCYANOGEN ($C_2NS_2=CyS_2$).—Liebig obtained this compound radical by saturating a concentrated solution of sulphocyanide of potassium with chlorine, as well as by boiling a soluble metallic sulphocyanide in diluted nitric acid. It falls in the form of a yellow precipitate, which preserves its color when dry; it is insoluble in water, alcohol, and ether, but soluble in hot sulphuric acid, from which it is again thrown down by water. It is decomposed by concentrated nitric acid: when heated with potassium—sulphide, cyanide, and sulphocyanide of potassium are formed; subjected to dry distillation, it yields sulphide of carbon, and ultimately nitrogen and cyanogen.

SULPHOCYANIC ACID. *Hydrosulphocyanic Acid* (CyS_2,H).—The aqueous solution of this acid may be obtained by decomposing basic sulphocyanide of lead by diluted sulphuric acid, taking care to leave excess of the salt of lead, which may be afterwards removed by sulphuretted hydrogen. It is also formed when sulphocyanide of lead or of silver, diffused through water, is decomposed by a current of sulphuretted hydrogen gas.

The hydrated hydrosulphocyanic acid is colorless, easily decomposed by exposure to air or heat, yielding, among other products, a peculiar yellow insoluble powder (*Mellone, see* page 262). Chlorine and nitric acid abstract its hydrogen, and evolve sulphocyanogen; by their prolonged action, cyanic and sulphuric acids are formed, and ultimately ammonia. It reddens the solutions of persalts of iron. It exists in a combined state in the seeds of certain cruciferous plants (mustard), and in the saliva of man and the sheep.

Sulphocyanides.—These salts are procured by neutralizing sulphocyanic acid with the respective bases, or by the action of hydrocyanic acid on polysulphides. The alkaline compounds are soluble in water and alcohol. They are identified by the deep red color which is produced, when a persalt of iron is added to their aqueous solutions. This reaction is employed for the detection of hydrocyanic acid (p. 269). The red color is destroyed by solutions of corrosive sublimate and chloride of gold. They give white precipitates with the salts of silver, and lead, and a gray precipitate with subsalts of mercury. The sulphocyanide of silver readily changes by light; it is not soluble in nitric acid, which gives a reddish color to the liquid, but it is dissolved by an excess of the alkaline sulphocyanide. Chloride of sodium produces no precipitate in this solution. The sulphocyanide of lead is soluble in nitric and acetic acids. With a salt of copper, a concentrated sulphocyanide gives a black precipitate: when diluted, a white sulphocyanide of the metal is slowly formed. When heated to a high temperature, a sulphocyanide is decomposed, yielding nitrogen, cyanogen, sulphide of carbon, and a metallic sulphide.

FERROCYANOGEN ($FeCy_3$=Cfy) and FERRICYANOGEN (Fe_2Cy_6,=Cfdy) are compound radicals, in which metallic iron is an important constituent. These will be again referred to in the description of that metal. *Ferrocyanides.*—The compounds formed with the alkalies are soluble in water, the others are insoluble. The soluble salts are yellow in the hydrated, and white in the dehydrated state. The persalts of iron give, with the soluble ferrocyanides, a deep blue precipitate (Prussian blue) 3Cfy,4Fe. The pure protosalts of iron give a white precipitate (protoferrocyanide of iron) becoming blue by exposure to air, oxygen, or chlorine. This has already been described as a valuable test for oxygen in water (page 91). Sulphate of copper gives, with a ferrocyanide, even in an extremely diluted state, a reddish-colored precipitate, ferrocyanide of copper (Cfy2Cu). The alkaline *ferri* or *ferridcyanides* are crystalline salts of a ruby-red color. They are recognized by the action of a protosalt of iron, which produces with them a blue precipitate (2Cfdy,3Fe). A persalt of iron darkens the solution, but there is no precipitate of Prussian blue. A crystal of an alkaline ferricyanide produces, with a mixture of strychnia and concentrated sulphuric acid, a splendid blue, passing to a purple and red color. No such results are produced when a portion of an alkaline ferrocyanide is employed.

Nitroprussides.—By the action of nitric acid on ferrocyanide of potassium, among other products, salts known as the nitroprussides are formed. This acid, like the ferrocyanic, is bibasic (*see* page 262). The salt of sodium ($Na_2Fe_2Cy_5,NO_2$) crystallizes in long red-colored prisms. It is soluble in water, but the solution is decomposed by light, Prussian blue being deposited. The test for a nitro-prusside, is a soluble alkaline sulphide, the smallest quantity of which produces a rich purple or crimson color, which, however, is not permanent (p. 214). The solution, although decomposed, is not colored by sulphuretted hydrogen alone.

Melam ($C_{12}N_{11}H_9$) is a product of the decomposition of sulphocyanide of ammonium.

Melamin ($C_6N_6H_6$) *Ammelin* ($C_6N_5H_5O_2$) and *Ammelid* ($C_{12}N_9H_9O_6$) are products of the decomposition of melam. They possess but little chemical interest.

CARBON AND SULPHUR. BISULPHIDE OF CARBON. SULPHOCARBONIC ACID (CS_2).—This is a liquid compound which was discovered in 1796 by Lampadius, while distilling a mixture of pyrites and charcoal; he termed it *alcohol of sulphur*. It may be obtained either by passing the vapor of sulphur over red-hot charcoal in a porcelain tube, or by distilling about six parts of yellow iron pyrites (bisulphide of iron) with one of charcoal. The charcoal should be in small fragments heated to full redness—the sulphur vapor slowly passed through it, and the refrigerator and receiver should be cooled to 32°, or even below. Vessels of porcelain and coated earthenware answer best, although it is difficult to prevent loss by the escape of the vapor; iron, at the high temperature which is required, too easily combines with the sulphur to render it conveniently available. The product is sometimes conveyed by a glass tube into ice-cold water.

When purified by redistillation at a low temperature with chloride of calcium, the bisulphide is a transparent, colorless liquid, insoluble in water, but soluble in alcohol and ether; its refractive and dispersive powers in regard to light are very considerable. Inclosed in a prismatic bottle it serves for the spectral analyses of the alkaline and other metals. Its specific gravity is 1·272. It boils at 110°, and does not freeze at —60°. It is very volatile and inflammable, and has a pungent taste and peculiarly fetid odor. The liquid poured on paper and inflamed, commonly burns with a blue flame without igniting the paper. When poured on water, a portion sinks in globules like a heavy oil, while another portion floats. This may be ignited, and in the pale flame, iron-wire burns with great brilliancy. If burnt on blue infusion of litmus, this liquid is reddened. The cold which it produces during evaporation is so intense, that by exposing a thermometer bulb, covered with fine lint, and moistened with it, in the receiver of an air-pump, the temperature sank, after exhaustion, to 80°. When a mercurial thermometer was used the metal froze. The intensity of the cold is such that it appears to have the power of freezing a portion of the liquid (*see* page 75). Asbestos or filtering paper placed in the liquid, soon acquires as a result of capillary attraction, a deposit of the solidified vapor. It is soluble in fixed and volatile oils, and it dissolves camphor, sulphur, phosphorus, and iodine. The readiness with which phosphorus dissolves in the bisulphide of carbon is remarkable, and the amount considerable—one part of the bisulphide taking up twenty parts of phosphorus. The solution is occasionally used to give a thin film of phosphorus to delicate articles intended to be coated with metals: they are dipped into it, and then into a solution of silver or copper, by which a film of the metal is reduced upon the surface: upon this other metals may be precipitated by the electric current. The solution of phosphorus is a powerful and often useful deoxidizer (page 221). When the vapor of bisulphide of carbon is passed over heated lime or baryta, it produces ignition, and carbonates of these bases, together with sulphides of calcium and of barium are formed. It is also decomposed by potassium, copper, and iron at a red heat. Under the influence of dry chlorine, it yields chloride of sulphur and perchloride of carbon.

The *vapor* of this liquid is very heavy, and may be decanted from one vessel into another. Pour the vapor into a small jar containing a solution of blue litmus, and ignite it: it will burn with a pale blue flame, producing sulphurous acid—known by its peculiar odor—and the litmus will be reddened. If a mixture of starch and iodic acid is placed in another jar, into which the vapor is poured and ignited, blue iodide of starch will be produced (page 202). The vapor is not decomposed by mere heat, but at a temperature of 600° it takes fire in air, and burns with explosion. Pour a small quantity of the liquid sulphide into a jar of 200 c.i. capacity, and after a few minutes, when the vapor is diffused, apply a lighted taper to it: the vapor will burn with a slight explosion producing a deposit of sulphur. It requires three volumes of oxygen for its perfect combustion; and sulphurous and carbonic acids are the only products ($S_2C+6O=CO_2+2SO_2$). As it is burnt in a jar, sulphur is deposited, the air not being in sufficient quantity to consume it.

Bisulphide of carbon appears to be frequently formed during the production of gas from coal, and to be retained in the state of vapor by the coal-gas after its purification by lime. This impurity gives a sulphurous smell to the gas when burned, although so perfectly deprived of sulphuretted hydrogen, as not to discolor carbonate of lead. The Rev. Mr. Bowditch has found that when coal-gas containing this vapor is passed over hydrate of lime, heated below the melting-point of lead, sulphide of calcium is produced, and sulphuretted hydrogen is set free; this gas may be subsequently separated by the hydrated oxide of iron. This is the only method which has yet been suggested for removing this noxious impurity from coal-gas. When the vapor of the bisulphide is burned with pure oxygen, it forms carbonic and sulphurous acids. It consists of

	Atoms.	Weights.	Per cent.	Vols.	Sp. Gr.
Carbon	1	6	15·79	1	0·4145
Sulphur	2	32	84·21	$\frac{1}{3}$	2·2112
Bisulphide of carbon	1	38	100·00	1	2·6257

The specific gravity of the vapor was found by Mitscherlich to be 2·640, which does not differ widely from that above given as the sum of the calculated specific gravities of its constituents. Compared with hydrogen, the vapor has a specific gravity of 38. It is analogous to carbonic acid, the two atoms of oxygen being replaced by two atoms of sulphur. Mr. Gore, who has compared the properties of the bisulphide, with those of *liquid* carbonic acid, finds that in solvent powers and general properties, they are analogous. The bisulphide is a more powerful solvent of fatty substances.

The vapor has been employed as an anæsthetic, but unsuccessfully. It is a narcotic poison. The liquid sulphide is manufactured on a large scale, and is extensively employed as a solvent of sulphur and caoutchouc, in the manufacture of vulcanized rubber. It is also used for the separation of phosphorus and iodine from organic substances in cases of poisoning. It will not combine with alkalies, but it forms a class of salts with the alkaline sulphides known as *sulphocarbonates*, represented by MS,CS_2. These resemble the carbonates which are MO,CO_2. It is obvious that, if according to the views of certain writers, a carbonate should be represented as M,CO_3, the sulphocarbonate would stand as M,CS_3, a change for which no sufficient reason has been offered. The vapor of this liquid furnishes a most powerful means of sulphuration. At a red heat, nearly all oxides are converted by it into sulphides (Fremy).

Tests.—The odor of the liquid, and the inflammability of the vapor, with the nature of the products of combustion, are sufficient to identify it. If pure, it should evaporate without leaving any residue. When the liquid is boiled with potassa containing oxide of lead dissolved, the presence of sulphur is indicated by the copious formation of brown sulphide of lead. It thus serves as a test for detecting the presence of oxide of lead as an impurity in a solution of potassa.

CHAPTER XXI.

BORON AND SILICON. BORACIC AND SILICIC ACIDS.

BORON ($B=11$).

BORON is a solid metalloid found only in combination with oxygen, as boracic acid. It was discovered by Davy as a constituent of this acid in 1807. Unlike carbon, it is an element which is but sparingly diffused, and is only found in the mineral kingdom. In the Lipari Islands and Tuscany it is deposited in the form of boracic acid; but in most cases it is associated with alkaline or alkaline earthy bases, either in mineral deposits or as a constituent of the waters of lakes and springs. Borate of soda or *tincal* is found in the waters of certain lakes in Ceylon, Thibet, and Tartary. Borate of lime, or *datholite*, is found in Norway, Sweden, and in South America, while borate of magnesia, or *boracite*, is met with in Holstein. The South American mineral is a compound borate, being a mixture of borate of soda and borate of lime ($NaO,2BO_3+2CaO,3BO_3+10HO$). It is found in Peru in white kidney-shaped masses, called *tiza*, associated with the deposits of nitrate of soda.

Preparation.—Boron may be procured in an amorphous state by heating anhydrous boracic acid finely powdered, to a temperature of about 300°, with twice its weight of potassium or sodium. The experiment may be performed in a copper or iron tube ($BO_3+3K=3KO+B$). This substance is also obtained by melting in a cast iron crucible, a mixture of 10 parts of anhydrous boracic acid, with 6 parts of sodium, and 4 or 5 parts of common salt. The salt aids the chemical changes, and forms an easily removable flux. The fused matter is washed out of the tube or crucible with water, and the whole put upon a filter. The boron remains in the form of a dark-colored, insipid, insoluble powder. The product is at first washed with diluted hydrochloric acid and then with water. Berzelius obtained boron by decomposing the borofluoride of potassium. This compound, in the state of dry powder, may be heated in a porcelain crucible with potassium; the reduction goes on quietly, and the fused mass may be triturated with water, by which the boron is separated. It is then washed upon a filter with a solution of hydrochlorate of ammonia, and afterwards with alcohol.

Wöhler and Deville obtained boron in a crystallized state, by heating, to a high temperature, in a plumbago crucible, for five hours, 8 parts of aluminum in large pieces, with 10 parts of anhydrous boracic acid. Boron and vitrified borate of alumina are produced. The metallic portion of the mass is treated with a boiling concentrated solution of soda, which removes the undecomposed aluminum; hydrochloric acid is subsequently added to remove the iron, and, lastly, nitrohydrofluoric acid to remove any silicon. In this process, aluminum passes to the state of alumina, at the expense of the oxygen of the boracic acid ($BO_3+2Al=Al_2O_3+B$). The boron thus obtained may, by repeated fusions with aluminum in excess, be obtained in hard crystals. These, however, retain both carbon and aluminum. By this process, Wöhler and Deville procured three varieties of crystallized boron: 1, black and opaque brittle laminæ, which have the lustre and nearly the hardness of the diamond; these crystals consist of 97·60 of boron, and 2·40 of carbon; 2, long prismatic crystals, perfectly transparent and as brilliant as diamond, but not so hard as the first variety; these crystals contain 89·10 boron, 6·70 aluminum, and 4·20 of carbon; 3, minute crystals of a chocolate-red or pale-yellowish color, of a sp. gr. of 2·68. These are boron diamonds. They are as hard as the diamond, and will scratch its surface.

Properties.—*Amorphous* boron is a deep olive-colored substance, infusible, inodorous, insipid, and a non-conductor of electricity. Its specific gravity exceeds 2. It is not acted upon by air, water, either hot or cold (at least after it has been heated to redness), alcohol, ether, or the oils. In the state of hydrate, it long remains diffused through pure water, especially if free alkali is present, and it even passes through filters; but its precipitation is accelerated by saline solutions (sal ammoniac). It undergoes no change when heated in close vessels; but when nearly red-hot in the air (600°), it takes fire and burns with difficulty into boracic acid, chiefly on the surface. According to Despretz, it becomes denser and more closely aggregated at a full red heat; and under a powerful galvanic battery, it has been fused into a black bead. It is more easily oxidized by the action of nitric acid: the pure hydracids at common temperatures have no action upon it, but nitrohydrochloric acid converts it into boracic acid, and nitrohydrofluoric acid into fluoride of boron. At a high temperature, it rapidly decomposes nitre with explosive violence; under the same circumstances, it also decomposes and deflagrates with the hydrate and carbonate of potassa: in the former case water is decomposed, and hydrogen evolved; in the latter, carbonic oxide is evolved in consequence of the decomposition of carbonic acid; in both cases borate of potassa is the result.

A boiling solution of potassa or soda has no action on boron. At a high temperature, boron deoxidizes most oxides and metallic salts. It inflames and burns in deutoxide of nitrogen, forming boracic acid and nitride of boron. It burns in chlorine, when slightly heated, and also in vapor of bromine, producing a chloride and bromide of boron. With hydrochloric acid it also produces a chloride, with the evolution of light and heat. At a full red heat it decomposes aqueous vapor, forming boracic acid and setting hydrogen free; a portion of the boracic acid is at the same time vaporized with water. Boron forms no compound with hydrogen, but it readily combines with nitrogen to form a nitride. This may be produced by heating the metalloid in a current of ammoniacal gas; hydrogen is liberated. When boron is heated in the vapor of sulphur, the two bodies combine to form sulphide of boron. The production of boracic acid in some of the hot springs of Tuscany, has been ascribed to the decomposition of sulphide of boron issuing with aqueous vapor from the volcanic soil. Boracic acid and sulphuretted hydrogen are among the products ($BS_3+3HO=BO_3+3HS$). When boron is strongly heated with boracic acid or borax, it fuses with the substance, producing a vitreous compound of a black or brown color, resembling smoky quartz. When very strongly heated in a close vessel, it acquires a chocolate-brown color, and closely resembles, in appearance, amorphous silicon. (WÖHLER and DEVILLE.) *Crystallized* or adamantine boron has been heated to the temperature at which iridium melts, without undergoing any change. Its sp. gr. is 2·68. It resists the action of oxygen at very high temperatures; but at the degree of heat at which diamond will enter into combustion, the boron diamond will burn in oxygen. Owing to the surface becoming rapidly covered with a layer of melted boracic acid, the combustion soon ceases. Chlorine combines with it at a red heat; and when a crystal of boron is heated between layers of platinum-foil, it combines with and causes the fusion of the metal.

BORON AND OYYGEN. BORACIC ACID (BO_3).—This acid, which is a crystalline solid, is the only known compound of boron and oxygen. It was first obtained by Homberg, in 1702, and was used in medicine under the name of *sedative salt*. Its composition was demonstrated by Davy in 1807. It is usually obtained by dissolving one part of borax in four parts of hot water, and subsequently adding half its weight of sulphuric acid. As the solution cools, white scaly crystals appear, which, when washed with cold water, are nearly tasteless; they consist of boracic acid combined with about 40 per cent. of water: they retain a portion of the acid employed, which may be driven off at a red heat. A hot saturated solution of borax may also be decomposed by hydrochloric acid ($NaO,2BO_3+HCl=NaCl+HO+2BO_3$): the hydrated boracic acid, which falls as the liquid cools, should be washed in cold water and dried. When it is heated in a platinum crucible, it fuses into a hard transparent glass, and by being thus heated, it loses any traces of hydrochloric acid which may be mixed with it. The following proportions will be found convenient for the production of the acid: 4 parts of borax dissolved in 10 parts of boiling water may be decomposed by 2½ parts of concentrated hydrochloric acid.

The specific gravity of the acid before fusion is 1·48, and after fusion 1·837. At a white heat, this acid slowly sublimes when exposed to air. It sometimes happens, that flashes of electric light are observed during the spontaneous cracking of a mass of fused boracic acid.

The *crystallized hydrate of boracic acid* ($BO_3,3HO$) is soluble in about 25 parts of cold, and 3 of boiling water. The latter solution, as it cools, deposits the acid in pearly scales; it is also soluble in pure alcohol, to the flame of which it communicates a beautiful green color. It is dissolved by several of the strong acids, especially the sulphuric. It has little taste, and feebly reddens vegetable blues; it renders turmeric brown like an alkali. The anhydrous acid (BO_3) becomes opaque when exposed to air; it is very fusible, and forms with many of the metallic oxides a glassy-looking substance variously colored; it is often used as a flux, and in the soldering of metals. Ebelmen has in this way employed it as a solvent of certain metallic oxides, which have afterwards been obtained from it in the form of crystals, so as to imitate native mineral products (*Ann. Ch. and Ph.* 3ème Sér. xxii. 211), such as the ruby and emerald. When boracic acid is perfectly pure, and is slowly deposited from its aqueous solution, it forms small prismatic crystals; it is more commonly seen in scaly crystals.

Composition.—Boron, when burned, or acidified by nitric acid, combines with about 68 per cent. of oxygen; and with this proportion the theoretical estimate of Berzelius coincides. There is, however a difference of opinion as to the atomic constitution of boracic acid, and the equivalent of boron. Boracic acid is generally represented as BO_3, and the equivalent of boron will thus be 10·8. Adopting 11 as the equivalent, anhydrous boracic acid will be constituted of

	Atoms.	Weights.	Per cent.
Boron	1	11	31·32
Oxygen	3	24	68·78
Boracic acid	1	35	100·00

The crystallized hydrate will consist of 56·4 anhydrous acid and 43·6 per cent. of water. The crystals of the acid, when dried at 212°, lose half their water.

Boracic acid is a feeble acid: it decomposes the solutions of the alkaline carbonates when moderately heated; but concentrated solutions of borates are decomposed by nearly all other acids. Owing to the fixed nature of boracic acid, it expels at a full red heat, the sulphuric and phosphoric acids from the sulphates and phosphates. It has no action on the alkaline chlorides, unless water is present, in which case a borate of the alkali is formed, and hydrochloric acid is set free. Hydrogen and carbon have no action upon the acid at the highest temperatures, unless chlorine is present. Under these circumstances the acid is decomposed and carbonic oxide and chloride of boron are produced ($BO_3+3C+3Cl=BCl_3+3CO$). It is deoxidized at a high temperature by potassium, sodium, and aluminum. The chief supply of boracic acid is from the district of Monte Cerboli and Sasso, in Tuscany. It is much employed as a flux for colors in the manufacture of porcelain.

Tests.—Boracic acid may be identified: 1. By its fusibility and fixedness at high temperatures; 2. By its sparing solubility in water and its entire solubility in boiling solutions of alkalies and alkaline carbonates, in the latter with effervescence; and 3. By its rich green color which it communicates to the flame of strong alcohol. Oxide of copper gives a similar tint, but this may be easily excluded.

Borates.—1. The alkaline borates are soluble in water, and have an alkaline reaction. 2. When the solution is concentrated by evaporation, if necessary, hydrochloric acid will throw down scaly crystals of boracic acid. 3. A salt of baryta throws down a white precipitate, soluble in nitric acid and even in an excess of water. 4. Nitrate of silver gives, with a soluble borate, if concentrated, a white precipitate, soluble in nitric acid; if diluted, a brown precipitate (oxide of silver). Arsenio-nitrate of silver gives a yellow precipitate with a borate, whether the solution is concentrated or diluted. These precipitates are soluble in nitric acid. 5. Sulphate of magnesia does not precipitate a concentrated solution of a borate in the cold; but white borate of magnesia is thrown down on boiling the mixture. 6. Add sulphuric acid to the borate, and then a small quantity of alcohol, ignite the mixture, and the appearance of a green flame will show the presence of boracic acid. This acid may be expelled from all minerals, by heating the powdered solid with a mixture of sulphuric and hydrofluoric acids. It escapes as fluoboric acid gas. A borate melts and forms a glassy-looking substance at a high temperature.

NITRIDE OF BORON (BN) has been already referred to. It is an amorphous white light powder. It was discovered in 1842 by Mr. Balmain, who gave to it the name of *Ethogen.* It is most readily obtained by heating to bright redness, in a platinum crucible, a mixture of two parts of dried sal ammoniac and one part of anhydrous borax, or an equivalent proportion of boracic acid. A white porous substance remains, from which the chloride of sodium may be removed by washing. It may also be procured by calcining a mixture of borax and ferrocyanide of potassium in a covered crucible.

The nitride of boron is an amorphous powder, insoluble, infusible, and fixed. It has neither taste nor smell. It burns under the blowpipe with a brilliant flame of a greenish-white color. When heated in a current of aqueous vapor, it produces ammonia and boracic acid (borate of ammonia). Heated with hydrate of potassa it yields ammonia. It is a powerful deoxidizer at a high temperature. Its most remarkable property is, that when calcined with dry carbonate of potassa, it yields borate and cyanate of potassa, so that it decomposes carbonic acid, the carbon of which unites with the nitrogen to form cyanogen ($BN+2(KO,CO_2)=KO,BO_3+KO,NC_2O$); if excess of the nitride is used, cyanide of potassium will also be formed. This appears to be the compound from which native boracic acid is sometimes formed in volcanic districts. Mr. Warington examined a substance brought from Vulcano, one of the Lipari Islands, and found it to possess all the properties of the artificial nitride of boron. Boracic acid was found condensed like drifted snow, within the crater of this volcano, and at a few inches below the surface, there was a mass of sal ammoniac. As ammonia is commonly found associated with native boracic acid, it is not improbable that these are products of the decomposition of nitride of boron by aqueous vapor ($BN+3HO=BO_3+NH_3$).

CHLORIDE OF BORON (BCl_3).—This is a volatile liquid compound of the two elements. It may be procured by passing dry chlorine over heated boron, or over a mixture of dry boracic acid and charcoal heated to redness. The vapor is here mixed with carbonic oxide ($BO_3+3C+3Cl=BCl_3+3CO$). The chloride is a highly refracting liquid of sp. gr. 1·35, boiling at a temperature of 59°. Its vapor has a density of 4·07. It is resolved by water into boracic and hydrochloric acids ($BCl_3+3HO=3HCl+BO_3$). There is a liquid bromide (B,Br_3) resembling the chloride.

FLUORIDE OF BORON. FLUOBORIC ACID (BF_3).—This is a gaseous compound, which may be obtained by heating a mixture of vitrified boracic acid and fluor-spar (fluoride of calcium) to whiteness; fluoboric acid passes over as a gas, and biborate of lime remains in the tube ($7BO_3+3CaF=3[CaO,2BO_3]+BF_3$). The gas may also be procured by heating in a glass retort, over a lamp, a mixture of 1 part of vitrified boracic acid, 2 parts of finely powdered fluor-spar, and 12 parts of sulphuric acid; but in this case, it is generally contaminated by fluosilicic acid gas, derived from the glass. It must be collected over dry mercury ($BO_3+3CaF+3(SO_3,HO)=3(CaO,SO_3)+3HO+BF_3$).

Fluoboric acid gas, according to Dr. Davy, has a specific gravity of 2·31; it is colorless, of a pungent, suffocating odor, highly deleterious when breathed, and it extinguishes flame. The gas strongly reddens litmus; and when bubbles of it are allowed to escape into the air, they produce remarkably dense white fumes, in consequence of their eager attraction for, and combination with aqueous vapor. It is thus a good test of humidity. Water takes up 700 times its volume of the gas, increasing in volume and density, and forming a caustic and fuming solution, in which Berzelius found boracic and hydrofluoric acids in combination (*borohydrofluoric acid*): it would seem, therefore, that fluoboric acid gas decomposes water, and that the hydrogen of the water unites to the fluorine to form hydrofluoric acid, and the oxygen to the boron, to form boracic acid ($BF_3+3HO=3HF+BO_3$.) When the solution is concentrated, the hydrofluoric and boracic acids again decompose each other, and the original compound is reproduced. Neither the gas nor the liquid acid act upon glass, but they speedily decompose almost all organic substances: a piece of paper introduced into the gas standing in a tall jar over mercury, causes its rapid absorption, and becomes charred as if burned, in consequence of the abstraction of the elements of water. When potassium is heated in fluoboric acid gas, it burns, and a brown compound results, consisting of boron and fluoride of potassium: the latter may be dissolved in water, and pure boron remains. The gas gives a green color to the flame of alcohol. It forms in equal volumes a solid white volatile compound with ammonia, both gases being in the anhydrous state. This compound is decomposed by water, and is converted into hydrofluate and borate of ammonia.

As the vapor densities of fluorine and boron are unknown, it is impossible to assign the volumetric constitution of the fluoride. The gas contains in 100 parts, by weight, 16·17 of boron and 83·83 of fluorine, or one atom of boron and three atoms of fluorine.

SILICON ($\mathrm{Si}=22$).

Silicon, like boron, may be obtained in the amorphous or crystalline state. It so closely resembles boron in one of its crystalline modifications (the graphitic), that the two metalloids cannot be distinguished by their appearance. In 1824, Berzelius first procured pure amorphous silicon, by decomposing at a high temperature, the silico-fluoride of potassium with an excess of the metal. Wöhler and Deville have since improved upon his process ; and they have first brought to the knowledge of chemists, that silicon might be procured in two, or, according to them, in three allotropic conditions—namely, the amorphous, graphitic, and the regular crystalline forms.

Preparation.—Amorphous or pulverulent silicon may be obtained by heating in an iron tube, a mixture of one part of the double fluoride of silicon and potassium ($\mathrm{3KF,2SiF_3}$) (or the hydrofluosilicate of potassa), with nine parts of potassium. (The double fluoride is itself obtained by saturating hydrofluosilicic acid with a strong solution of potassa, washing the precipitate, and drying it thoroughly below a red heat.) In heating the mixture, the mass becomes suddenly incandescent, and the following changes take place: $(\underbrace{\mathrm{3KF,2SiF_3}}+\mathrm{6K}=\mathrm{9KF}+\mathrm{2Si})$. The residue, when cooled, is treated with cold water, some hydrogen escapes from the decomposition of a portion of silicide of potassium, formed in the process, and silicon is precipitated in an insoluble form. After the liquid, used in washing the precipitate, ceases to be alkaline, hot water is employed in order to remove any undecomposed double fluoride ; and the silicon remains as a dark brown powder. The decomposition of the vapors of the fluoride and chloride of silicon, in passing them through a heated tube containing potassium or sodium, furnishes other methods of procuring this metalloid.

The most economical process for obtaining *crystallized* silicon, according to CARON, is to project quickly into a red-hot crucible (provided with a cover, also kept red-hot) a mixture of 30 parts of dried silico-fluoride of potassium, with 40 parts of pure granulated zinc, and 8 parts of sodium, in small pieces. The mass is removed from the crucible when cooled ; and while the lower part contains the ingot of zinc, the crystallized silicon will be found adhering to the upper portion of this metal. The greater part of the zinc is run out by raising the mass to its melting-point; and the small quantity which adheres to the silicon, and any iron that may be present are removed by digesting the mass in concentrated hydrochloric acid. If lead is present, this should be removed by nitric acid; the pure silicon which remains, may be washed and dried. The silicon thus obtained may be melted by mixing it with the double fluoride and coarsely-powdered glass, and heating the mixture in a double crucible to the melting-point of iron. A globule of silicon is formed in the midst of the glass and slag. These substances may be removed mechanically, and any adhering traces, by immersing the silicon in concentrated hydrofluoric acid, which has no action on this substance.

The scaly crystals, or graphitic silicon, were obtained by Deville in decomposing the dry double fluoride by aluminum, at the melting-point of silver: silicide of aluminum was produced. This compound, treated first with boiling hydrochloric acid, and afterwards with hydrofluoric acid, left pure silicon in scales resembling graphite : the aluminum and any silica produced in the process, being completely removed by the two acids $(\underbrace{\mathrm{3KF,2SiF_3}}+\mathrm{5Al}=\mathrm{3KF}+\mathrm{2Al_2F_3}+\mathrm{Al2Si})$. 100 parts of aluminum gave by this process from 30 to 80 parts of silicide, containing from 65 to 75 per cent. of its weight of silicon. The aluminum appears to determine the crystalline form of the silicon, under these circumstances, just as cast-iron affects carbon, in producing artificial graphite. In decomposing the vapor of chloride of silicon by aluminum in a vessel containing hydrogen, Wöhler and Deville obtained silicon in hard hexahedral prisms of an iron-gray color, and of a reddish tint, by reflection. These crystals, like diamond, had the property of scratching glass, and even cutting it.

Properties.—Amorphous silicon is a dark brown powder, less fusible than boron, but still capable of being melted between the poles of a powerful voltaic battery, or by fusion, as in the process above described. It is insoluble in water, hot or cold. It is a non-conductor of electricity. Nitric, hydrochloric, and sulphuric acids, whether separately or mixed, have no action upon it, even when boiled. It may be exposed to a very high temperature in close vessels, without any other change than an increase of hardness and density; but if heated in air or oxygen before it has been thus calcined in close vessels, it will take fire, and burn superficially, the silicic acid formed melting and protecting the residuary silicon from continued combustion. A full red heat in a covered platinum crucible, appears to produce an allotropic change in this substance. Pulverulent silicon, in the amorphous state, decomposes cold hydrofluoric acid, as well as a concentrated hot solution of potassa, hydrogen being liberated in both cases, and silicon dissolved. A fluoride is formed with the acid, and a soluble silicate with the alkali. Silicon, heated to full redness, acquires so great a density, that it sinks in sulphuric acid; and it loses the property of burning in oxygen or air, even when heated in the flame of the blowpipe. Hydrofluoric acid and a boiling solution of potassa are not decomposed by it; but nitro-hydrofluoric acid alone dissolves it, with the evolution of deutoxide of nitrogen. (FREMY.)

When heated with an alkaline carbonate at the temperature of fusion, a silicate of the alkali is formed, carbonic acid is decomposed, and carbonic oxide escapes. If the silicon is in large proportion, this gas is even deoxidized, and carbon is set free. This shows that silicon has a stronger affinity for oxygen than carbon, and that its deoxidizing powers are equal to those of the alkaline metals. It does not decompose nitrate of potassa at a dull red heat, unless this salt is mixed with a portion of carbonate, when deoxidation takes place with explosive violence. At full redness decomposition is produced without the addition of the carbonate. It is oxidized by the hydrated alkalies in the melted state, but it has no action on boracic acid or borax, at the temperature of fusion. When heated in a current of chlorine, it undergoes combustion and forms a volatile chloride. It fuses with platinum, when melted in this metal, or as it is evolved in the nascent state. It is said to combine with hydrogen, to form a gaseous silicide of hydrogen. This gas is spontaneously inflammable in air, like phosphide of hydrogen, burning with a bright white flame, and producing wreaths of vapor of white silicic acid. The gas is decomposed at a red heat, silicon being deposited, and it detonates violently when mixed with chlorine. Its constitution has not been determined.

Crystallized silicon in the graphic state, possesses most of the chemical properties assigned to amorphous silicon which has been intensely heated. It has the color and lustre of iodine, is very hard, and has a specific gravity of 2·49. It is a good conductor of electricity. It is insoluble in all acids excepting the nitro-hydrofluoric. It decomposes fused carbonate of potassa at a red heat; and, at the same temperature, burns in chlorine, forming a chloride.

SILICON AND OXYGEN. SILICIC ACID (SiO_3). *Silica.*—This is an abundant natural product. It is a constituent of every soil, and is found more or less in all spring, river, and sea-waters. Under the form of sand and *sandstone*, it covers a large portion of the surface of the earth, and it is found in all rocks, from the most ancient to the most recent. Granite, felspar, and all the varieties of natural clays, contain a large proportion of silicic acid in combination with alumina, oxide of iron, lime, magnesia, and other bases. While carbon, the first member of this group of metalloids, is the main constituent of the organic, silicon, in the form of silicic acid, is the chief constituent of the inorganic kingdom. It is, however, not an unimportant constituent of organic matter. The cuticle or epidermis of the grasses, and of the husks of grains, is constituted of silicic acid. The cuticle and scaly hairs of *Deutzia* contain a large quantity of this substance. In the *Equisetaceæ*, the whole structure of the vegetable is so penetrated by it, that a complete skeleton of the vegetable structure in silicic acid, may be obtained. Silica is found, more or less, in the ashes of all vegetables, especially of those which grow on sandy soils. In some species of plants it forms 13 per cent., and in others 50 per cent. of the ash. According to Johnston, it forms 65 per cent. of the ash of wheat-straw, and 74 per cent. of that of rice-straw. In the bamboo (*Bambusa arundinacea*) silica is often collected at the joints in masses: and to these the name of *tabasheer* is given. The long, slender, and hollow stems of the grasses, derive their strength from their silicious covering. The silica is generally deposited in plates, grains or needles: on the leaves of *deutzia scabra*, it is deposited in a stellated form.

It is but sparingly diffused in the bodies of man, and the higher orders of animals; but it constitutes the skeleton of whole tribes of infusoria. The substance called mineral flour, or *mountain-meal* (*Bergmehl*), is almost entirely constituted of the silicious skeletons of infusoria. A specimen of this substance, obtained by Dr. Traill from Swedish Lapland, and analyzed by him, was found, in the dry state, to consist of 71·13 parts of silicic acid, 22 of organic matter, 5·31 of alumina, and 0·15 of oxide of iron. The cells of the *Diatomaceæ* have silicious coverings, which enable them to retain their form, even after digestion in strong acids.

The following are the principal minerals which contain silicic acid (silica), pure, or nearly so.

Rock-crystal, or *quartz*, which may be considered as pure anhydrous silicic acid (silica). It crystallizes in the form of a six-sided prism, terminated by six-sided pyramids. Some varieties are perfectly transparent and colorless; others white (milk-quartz) and more or less opaque. Its specific gravity is 2·6. It is so hard as to give sparks when struck with steel, and is nearly infusible. The primitive crystal, which is rare, is an obtuse rhomb, the angles of which are 94° 24′, and 85° 36′. The finest and largest specimens of quartz are brought from Madagascar, the Brazils, and the Alps. The small and perfectly transparent crystals found near Bristol and in Cornwall, are sometimes called *Bristol and Cornish diamonds.* The finest crystals are cut into ornaments, and are used as a substitute for glass in spectacles; they are then termed pebbles; they are harder and do not so readily become scratched as glass. The refractive power of rock-crystal is the same as that of glass, being about 1·6. Water is 1·3, and the diamond 2·47. Owing to this difference, the lustre and brilliancy of rock-crystal is far inferior to that of diamond. Quartz is also of lower specific gravity, and although hard enough to scratch glass, its surface is easily scratched by the diamond, as well as by the topaz and ruby. Brown and yellow crystals of quartz are found in great beauty in the mountain of Cairn Gorm, in Scotland. This variety of quartz is sometimes called Scotch topaz; it varies in color from a pale yellow to a deep amber tint. The color may be due to the presence of traces of carbon or silicon. The *brown quartz* varies much in shade from a smoky to a very deep tint: the color is probably due to a similar cause. Fine samples of smoky quartz are found in Switzerland. Purple quartz, or *amethyst*, is found in India, Ceylon, and Persia: it owes its color to traces of iron and manganese. Rose-quartz derives its color from manganese. *Prase*, or green quartz, is colored with oxide of iron; and *chrysoprase* is tinged of a delicate apple-green by oxide of nickel. *Aventurine* is a beautiful variety of quartz, of a rich brown color, which is filled with bright spangles of golden mica; the finest specimens are from Cape de Gatte in Spain. The artificial aventurine is a variety of glass, containing tetrahedral crystals of metallic copper produced by fusion. Small crystals of quartz, tinged with iron, are found in Spain, and have been termed hyacinths of Compostella.

Chalcedony, *Carnelian*, *Onyx*, *Sardonyx*, and *Blood-stone*, or *Heliotrope*, and the numerous varieties of *Agates*, are principally composed of quartz, with various tinging materials, chiefly oxide of iron. *Flint* owes its black color apparently to organic matter. When heated in a current of air to a very high temperature, it yields white amorphous silicic acid, nearly pure, with a trace of oxide of iron.

Opal is among the most beautiful productions of the mineral world; it is a compound of about 90 silicic acid and 10 water, and is distinguished by its very brilliant play of iridescent colors. The finest specimens come exclusively from Hungary. There is a variety of opal called *hydrophane*, which is white and opaque until immersed in water; it then resembles the former. The proportion of water with which silica is combined in the different varieties of opal, is liable to so much variation, that they can scarcely be regarded as definite hydrates.

Common opal is usually of a dirty white color, and does not exhibit the colors of the noble opal; it contains silicic acid and water, with a little oxide of iron, and is not of unfrequent occurrence. *Wood-opal* is opaque, of a brown color, and of a ligneous appearance. *Jasper* is a perfectly opaque variety of silica, containing oxide of iron, and of a red, brown, or green color; these colors often alternating and giving a striped appearance to the substance. Black jasper, or Lydian quartz, forms the touchstone of jewellers.

The term *chalcedony*, from Chalcedon in Bithynia, near to which it is found in large quantity, is applied to a variety of bluish and translucent stalactitic quartz, sometimes of a milk-white or a gray color. The milk-white variety forms white carnelian, and the red variety forms red carnelian. When brown and opaque-white chalcedony occurs in alternate layers, it constitutes the *onyx*. If the color is of a deep brownish-red, or by transmitted light, blood-red, the stone is termed *sard*. Alternate layers of sard and milk-white chalcedony, constitute *Sardonyx*. *Heliotrope* has a deep green color: it derives its name of blood-stone from the bright red spots of peroxide of iron scattered through it. It is found in Siberia and Iceland. (THOMSON.) *Mocha-stone* is chalcedony containing dendrites, usually of a black or brown color; but sometimes green, and resembling certain mosses. Hence the term *moss-agates*. The filaments which have the appearance of vegetable fibres appear to be owing to the infiltration of iron, manganese, or their compounds. Mocha-stone is chiefly brought from Arabia. *Agate* has a basis of chalcedony, with sometimes crystals of quartz or amethyst in the centre. It consists of alternate layers of chalcedony, quartz, jasper, heliotrope, or opal, the layers being occasionally disposed in an angular form (fortification agates) and variously colored. It is found in Saxony, Bohemia, Siberia, Iceland, and the Isle of Skye. This substance is useful to the chemist, as it is turned into mortars for grinding hard substances. The order of hardness usually adopted by mineralogists is as follows: 1. talc; 2. gypsum; 3. calcareous spar; 4. fluor-spar; 5. phosphate of lime; 6. felspar; 7. quartz; 8. topaz; 9. sapphire and ruby; 10. diamond. The diamond can only be powdered in hard steel mortars. When once reduced to fragments by cleavage, its own powder serves for its further trituration.

Obsidian is a glassy-looking substance, of a greenish or brownish-black color. It is found in the Lipari Islands and Iceland. It is *volcanic-glass*. It contains from 72 to 78 per cent. of silicic acid combined with alumina, potassa, and soda. It owes its color to oxide of iron. *Pumice* is a porous fibrous substance of a gray color. It contains 77·5 per cent. of silicic acid. It is found chiefly interstratified with obsidian in the islands of Lipari and Ponza. In Lipari, there is a hill (*Capo Bianco*) 1000 feet high, constituted entirely of pumice.

Tripoli contains 90 silicic acid, 7 alumina, and 3 of oxide of iron. It was formerly brought from Tripoli in Africa, whence its name. It is found in Bohemia and Tuscany. When finely levigated by trituration with water, it is much used for polishing metals, marble, glass, and other hard bodies.

Preparation.—Silicic acid may be obtained for chemical purposes by the following process. Heat colorless rock-crystal to redness, quench it in water, and reduce it to a fine powder; in this state it is silicic acid, almost perfectly pure. Fuse 1 part of this powder with 3 parts of a mixture consisting of equal parts of carbonate of soda and carbonate of potassa, in a silver or platinum crucible. Dissolve the resulting mass in water, add a slight excess of hydrochloric acid, and evaporate to dryness. Wash the dry mass in boiling distilled water upon a filter, and the white substance which remains is silica. This is the usual process. The silica obtained by simply reducing the colorless rock-crystal to powder is nearly pure: it sometimes contains traces of oxide of iron and manganese, as well as of alumina. Pure silica may also be obtained, by the fusion of fine white sand, or powdered rock-crystal, with carbonate of lime: the resulting compound of lime and silica may be decomposed by dilute hydrochloric acid, and the product, after having been duly washed, is silica in the form of a light powder. When gaseous fluoride of silicon (fluosilicic acid) is passed into water, the silicic acid which is precipitated, after having been washed and dried, is also pure, and in a state of extreme mechanical division.

At a high temperature, steam carries off silica in the state of vapor, thus establishing an analogy between the silicic and boracic acids. While boracic acid is fusible at a red, and volatile at a white heat, silicic acid, according to Deville, is less fusible than platinum, but is volatile at this temperature in a current of gas or vapor.

Properties.—Silicic acid exists in two states, the *amorphous* and *crystalline*. The acid obtained by precipitation in the processes above described, is the amorphous variety; while the native rock-crystal represents the crystalline form. They are differently affected by reagents. Amorphous silicic acid, as it is precipitated from its solutions, is supposed to be a hydrate, represented by the formula, SiO_3,HO.—When dried at 212°, it is said to lose half its water, and to become $2(SiO_3)HO$. According to Mitscherlich, there is no definite hydrate of silicic acid. It loses a variable quantity of water in drying, and absorbs water in a damp atmosphere. When the precipitate is heated to 370°, it loses the whole of its water, and forms the insoluble variety of amorphous silicic acid (SiO_3). In this state, it is a white, tasteless powder, insoluble in water, and not forming with it a cohesive, plastic mass, like alumina. It has no action on vegetable colors, and is infusible except under the intense heat of the oxyhydrogen blowpipe, in the flame of which it melts, forming a transparent colorless globule. Its sp. gr. is, like that of the crystalline variety, 2·66. It is not dissolved by any of the oxacids, either separately or in mixture, even at a boiling temperature. When a very diluted solution of a silicate is treated with sulphuric, hydrochloric, or nitric acid, the silicic acid is not precipitated, but appears to be dissolved by the water as a hydrate. When the acid solution is, however, concentrated by evaporation, or the acid is at once added to a concentrated solution of a silicate, the hydrate is precipitated in a gelatinous form, and when dried and strongly heated it forms the insoluble variety.

Solubility of Silicic Acid.—The solubility of silicic acid in water has been hitherto doubted or denied by chemists. Some have admitted that pure water would dissolve only a thousandth part of its weight of recently precipitated, or gelatinous silica. Mr. Graham has, however, by the process of dialysis, succeeded in procuring a solution of silica varying from 5 to 14 per cent. of the weight of the water. He added hydrochloric acid to a solution of silicate of soda, and placed the mixture in a dialyser (p. 133). In a few days the chloride of sodium and hydrochloric acid were entirely removed, while silica and water alone remained in the dialyser. He calls this *colloid* silicic acid. The liquid, when left to itself, slowly deposited silica in a gelatinous and insoluble form: hence it cannot be regarded as a solution in its proper chemical signification (pp. 45—47). Lime-water, or a solution of carbonate of potassa, added to it, rapidly caused the separation of silicic acid in a gelatinous form. These facts may account for the temporary solubility and deposit of silica, under circumstances which have hitherto appeared difficult of explanation.

Amorphous silicic acid, either in the state of gelatinous hydrate, or in powder dried but not heated, is readily dissolved in the cold by concentrated hydrochloric, nitric, or sulphuric acid. A strong solution of potassa or soda will dissolve it, but with more difficulty. In evaporating alkaline solutions in glazed porcelain dishes, a portion of the silica of the glaze is frequently dissolved. The alkalies also dissolve silica from flint glass.

Silicic acid which has been strongly calcined, is as insoluble in alkalies and oxacids as the anhydrous native silicic acid—rock-crystal. Among hydracids, the hydrofluoric is the only one which dissolves silicic acid, forming water and fluoride of silicon ($SiO_3+3HF=3HO+SiF_3$). The rapidity of this action is in proportion to the concentration of the acid. If the silicic acid is in fine powder, if it has not been calcined, and if a sufficient quantity of hydrofluoric acid is employed, it is readily dissolved. Insoluble silicates, such as the varieties of glass, are similarly attacked and dissolved by this acid; but crystalline silicic acid, or native rock-crystal, resists its action.

In the precipitation of silicic acid from its alkaline solutions by acids, alumina may be associated with it. If the residue is brought to dryness, moistened with strong hydrochloric acid for half-an-hour, and then boiled in water, alumina, as well as oxide of iron, magnesia, and other bases present, will be entirely dissolved, while the silicic acid alone will remain undissolved. Its quantity may thus be determined.

Silicic acid is precipitated from its concentrated solutions by nearly all acids, even the carbonic and hydrocyanic. When its solutions are long kept, or are exposed to air, the silicic acid is deposited as an opaque white mass. The silica thus precipitated is readily dissolved by strong acids, but not readily by alkaline solutions, even at a boiling temperature. When dry silicic acid is fused with the hydrates of potassa, soda, or baryta, it readily enters into combination, forming silicates. In the anhydrous state, at a high temperature, it expels carbonic acid from alkaline carbonates (KO,CO_2

$+SiO_3=KO,SiO_3+CO_2$). It is worthy of remark, that in this decomposition, there is no substitution of a metallic oxide for water, but a displacement of one anhydrous acid by another. It is impossible to regard silicic acid as a salt of hydrogen. It is an anhydrous oxacid, capable of displacing other oxacids at a high temperature, without the intervention of the elements of water.

Silicic acid is unaffected at the highest temperatures by hydrogen, carbon, phosphorus, or chlorine. When, however, it is heated and exposed to the combined action of chlorine and carbon, oxide of carbon and a volatile chloride of silicon are produced. When heated with carbon in contact with iron or platinum, it undergoes decomposition: carbonic oxide escapes, and silicides of the metals result. Platinum vessels may be thus destroyed by nascent silicon.

Although silicic acid, as it is commonly met with, is not soluble in water, yet there is scarcely a river or spring-water in which traces of it may not be found. It appears to be held in solution either by alkalies or their carbonates. The *Geyser* springs of Iceland contain a large quantity of silicic acid. We have found as much as 48 grains in a gallon of the water of the *Great Geyser* (1856): the solvent here appears to be carbonate of soda, the effect of which is probably aided by the high temperature as well as the pressure to which the heated column of water is subjected. The silicic acid is precipitated from the water in a hard crystalline form on all the surrounding rocks. It has been already stated that hydrated silicic acid may be volatilized with aqueous vapor at a high temperature, like hydrated boracic acid (p. 283).

Composition.—The amount of oxygen contained in 100 parts of silicic acid, has been variously estimated at from 51·98 (MITSCHERLICH) to 52·93. Assuming the former proportion to be correct, and silicic acid to contain 3 atoms of oxygen united with 1 atom of silicon (SiO_3), then (51·98 : 24 : : 48·02 : 22·1) the equivalent of silicon would be 22. This is in accordance with the views of Berzelius and the majority of British and foreign chemists, including the most recent writers on the subject, Pelouze and Frémy. It is also consistent with the atomic constitution of boracic acid, to which silicic acid bears a much stronger analogy in chemical and physical properties, than it does to the oxygen compound of carbon (CO_2). It has, however, been proposed to alter the equivalent of silicon, by making the formula of silicic acid SiO_2; but there are no valid reasons for making this change. Col. York, in experimenting with silicic acid on different alkaline salts and bases, obtained such widely different results, that he could draw no satisfactory conclusion. Thus, in calculating by the amount of carbonic acid expelled by silicic acid from fused carbonate of potassa, the mean result of four experiments gave as the equivalent of silicic acid 30·7, corresponding to the formula SiO_2. Seven experiments with the carbonate of soda, however, gave an equivalent of 21·3, represented by SiO_3. Carbonate of lithia gave the number 14·99, nearly agreeing with the formula SiO. The fusion of silicic acid with hydrate of potassa gave a result corresponding to that derived from the carbonate, 30·8; but hydrate of soda gave 17·2, a result approaching to that obtained by carbonate of lithia. Such results furnish no grounds for changing the equivalent of silicic acid. On the other hand, in experimenting with other substances, this gentleman found that boracic acid only, gave results similar to those obtained with silicic acid. (*Proc. R. S.*, Vol. 8, No. 25, p. 441.) As this acid is admitted to have the formula of BO_3, this simple fact justifies the retention of the generally accepted formula, SiO_3. Apart from other strong analogies between boron and silicon, a change in the formula of silicon would be, therefore, inexpedient and inconsistent.

The recent experiments of Scheerer (*Chem. News*, March 30, 1861, 205) show that, in fusing silicic acid with carbonate of soda, various silicates may be produced, and variable amounts of carbonic acid expelled. The result depends on the temperature of fusion, the duration of the fusion, the relative proportions of silicic acid and base, and the chemical relations of carbonic acid to the base at a high temperature. From his results, Scheerer considers the formula SiO_3 to be correct.

Silicates.—These salts form a numerous class of substances, in some of which the acid, and in others the base, predominates. All are insoluble in water, excepting those of potassa and soda. The polysilicates of these alkalies constitute varieties of glass. The aqueous solution of a soluble silicate is alkaline. It gives a white precipitate with ammonia, or carbonate of ammonia, which is not dissolved by a cold solution of potassa, or by chloride of ammonium. (A precipitate given by carbonate of ammonia in a salt of alumina is dissolved by a cold solution of potassa.) A silicate is distinguished from the alkaline-earthy and all other salts, by the fact that an acid (even the acetic) will precipitate the silicic acid from a concentrated solution, as a gelatinous hydrate. The white powder obtained on drying and heating this precipitate, may be identified as silicic acid, by its insolubility in all menstrua excepting hydrofluoric acid. It is dissolved by this acid, and if the silicic acid contains no impurity, the whole of it may be volatilized as fluoride of silicon, by heating the solution in a platinum capsule.

Among other chemical characters of a soluble silicate, may be mentioned the following. Nitrate of silver gives with the solution a brown, and the arsenio-nitrate a yellow precipitate. It is precipitated in a gelatinous form by all the salts of ammonia, and by all acids, including even the hydrocyanic and carbonic. Nitrate of baryta also produces in it a gelatinous precipitate which is not dissolved by nitric acid; but this could not be mistaken for a sulphate, inasmuch as nitric acid alone, produces a dense gelatinous precipitate in a solution of a silicate.

The analysis of the *insoluble* silicates is attended with some difficulties. Some of these in which the base predominates, as in certain slags, may be entirely decomposed, and the silicic acid set free in a gelatinous form, by digesting the finely powdered silicate in a strong acid, such as the sulphuric, hydrochloric, nitric, or even the acetic. The bases are found in soluble combination with the acid, which should be selected accordingly. The greater number of native silicates admit, however, of being correctly analyzed only by fusion. The silicate, very finely powdered, may be mixed with four times its weight of a mixture consisting of equal parts of the carbonates of potassa and soda, and fused in a platinum crucible for half an hour. When cold, the residuary mass may be digested in an excess of hydrochloric acid, and gently heated. If the decomposition of the silicate has been complete, no insoluble gritty matter will remain. When the whole is dissolved, the acid liquid is evaporated to dryness, the residue moistened with concentrated hydrochloric acid, and after a time boiled in water. The solution is filtered; the silicic acid, collected on the filter, is well washed and dried. The bases associated with the silicic acid will be found in the filtered liquid. The hydrates of potassa or soda act more readily by fusion, but the process cannot be carried on in platinum. If the silicic acid is combined with potassa or soda, the powdered silicate may be fused either with pure baryta, or the carbonate or nitrate of this alkaline earth. All the insoluble silicates fuse at a high temperature, and more readily when mixed, than when separate.

Silicic acid is often associated with *titanic acid.* In order to separate this, the silicate may be fused in a platinum crucible, with bisulphate of potassa. The titanic acid may be dissolved out of the residue by water, while the silicic acid will remain undissolved. (WILL.)

Wöhler and Buff have described a hydrated sesquioxide of silicon (Si_2O_3, 2HO) as a light, white, amorphous substance, obtained by the action of water on the hydrochlorate of the chloride of silicon.

CHLORIDE OF SILICON ($SiCl_3$).—Silicon burns when heated in a current of dry chlorine, producing this gaseous compound. It may be produced by passing dry chlorine over silicon heated to redness, or by passing the dry gas over a mixture of silicic acid and charcoal similarly heated ($SiO_3+3C+3Cl=SiCl_3+3CO$). The chloride is a yellowish fuming liquid of a sp. gr. of 1·52, boiling at 122°, and converted by water into hydrochloric and silicic acids ($SiCl_3+3HO=SiO_3+3HCl$). Its vapor has a density of 5·939. Each volume contains two volumes of chlorine. There is also a Bromide of Silicon ($SiBr_3$).

FLUORIDE OF SILICON. (SiF_3). *Fluosilicic Acid.*—The only body which acts energetically upon silicic acid is the hydrofluoric acid: the result of this action is a gaseous compound. To obtain the gaseous fluoride of silicon, four parts of pulverized fluor-spar and three of powdered glass, or two of silica finely powdered, are well mixed in a retort with about five parts of oil of vitriol; the gas evolved is to be collected over mercury, and when its production slackens, it may be accelerated by a gentle heat. The mercury and the glass vessels employed must be quite dry, for if in the least damp, they acquire an adhering film of silica. This decomposition depends upon the evolution of hydrofluoric acid and its action upon the silica, water and fluoride of silicon being the ultimate results ($SiO_3+3HF=SiF_3+3HO$). The hydrofluoric acid is derived from the action of the aqueous sulphuric acid on the fluoride of calcium; $CaF+SO_3,HO=HF+CaO,SO_3$.

Fluoride of silicon is a colorless gas; its odor is acrid, somewhat resembling that of hydrochloric acid; its taste very sour; its specific gravity is 3·6 compared with air; 100 cubic inches weigh nearly 112 grains. It extinguishes the flame of a taper, and all combustible bodies: it has no action on glass; it may be liquefied and solidified by cold. It produces white fumes when in contact with damp air; and when exposed to water it is absorbed, and a soluble compound of silicic with hydrofluoric acid is formed. The changes may be thus represented: $3SiF_3+3HO=3HF,2SiF_3+SiO_3$. The hydrofluosilicic acid, $3HF,2SiF_3$, is dissolved in the water, while the silicic acid SiO_3, is precipitated in a gelatinous state. If the beak of a retort from which the gas is issuing, is plunged into a basin of water, it will be soon choked by a copious deposit of hydrated silica, which sometimes forms tubes through the water, by which the gas escapes directly into the air. Water will dissolve 350 volumes of this gas, and when it is intended to make a solution, or to produce gelatinous hydrate of silica, the conducting tube or beak of the retort should be so fixed as to plunge just below the level of a small quantity of mercury in a conical glass. Water may be carefully poured on the mercury, until the glass is filled, and the distillation then safely carried on. As each bubble of the fluoride of silicon escapes through the mercury and rises into the water, it becomes invested with an envelope of the hydrate of silica, owing to the decomposition above described.

This gas is dissolved by alcohol, but if the alcohol is hydrated there is a separation of silicic acid. The decomposition of this gas by water, enables a chemist to detect the slightest trace of silicic acid in any mineral. The mineral should be powdered and mixed with powdered fluor-spar (free from silica) and sulphuric acid. The mixture should be heated in a platinum vessel, and the vapors carried by a platinum tube into water. If silica is present in the mineral, there will be a separation of the gelatinous hydrate, on contact with the water. The whole of the silicic acid may be thus expelled.

When a streak is made on paper with a solution of fluosilicic acid, the paper is not carbonized when heated. If sulphuric acid is present as an impurity, the paper will be carbonized.

Hydrofluosilicic Acid ($3HF,2SiF_3$).—This is a product of the decomposition of the fluoride above-mentioned, in contact with water. The acid may be procured by separating the gelatinous silica, by means of a linen filter, and filtering the liquid through paper. It is also produced when diluted hydrofluoric acid is saturated with silica.

The liquid has a strongly acid reaction. It may be evaporated in a platinum vessel without change, but it corrodes glass; and, when highly concentrated, it is converted into hydrofluoric acid, and silica, which is deposited. Although its solution has no direct action on glass, it slowly acts upon the alkaline bases, potassa, soda, lime, and oxide of iron existing in glass, and forms a white deposit of a hydrofluosilicate of the base. Its action on alkalies and their salts is remarkable. It precipitates in an insoluble form as *hydrofluosilicates* or double silicofluorides ($3MF,2SiF_3$), potassa, soda, and baryta. Pure lime and strontia are not precipitated from their solutions in water. Ammonia in excess and carbonate of ammonia, decompose the acid and throw down gelatinous silica. Concentrated solutions of the *salts* of potassa, soda, lithia, baryta, and alumina, are also precipitated; those of potassa so completely, that the alkali may be thus separated from the acid. In this manner chloric acid may be obtained by adding hydrofluosilicic acid to a strong solution of chlorate of potassa (p. 179). In these cases the hydrogen of the acid is simply replaced by the metal. A solution of the acid precipitates a salt of strontia, but much more slowly than a salt of baryta. These precipitates, like those given by sulphuric acid in the solutions of the alkaline-earthy salts, are insoluble in nitric acid, and might be mistaken for sulphates. When calcined, they leave a fluoride, which may be identified by its action on glass. A sulphate is only decomposed when heated with charcoal, or cyanide of potassium, and a sulphide then results.

Silicon forms compounds with nitrogen and sulphur, SiN_3(?), and SiS_3.

METALS.

CHAPTER XXII.

PHYSICAL PROPERTIES OF THE METALS. RELATIONS TO HEAT, LIGHT, ELECTRICITY, AND MAGNETISM.

THE metals constitute a numerous and important class of elementary bodies; they are characterized by a peculiar and distinctive lustre, by their opacity, and by their high conducting powers in regard to heat and electricity. In the following table they are enumerated in the order in which they will be described. A table of their symbols and equivalents will be found at page 63.

POTASSIUM
SODIUM
LITHIUM
CÆSIUM
RUBIDIUM

BARIUM
STRONTIUM
CALCIUM
MAGNESIUM

ALUMINUM
GLUCINUM
ZIRCONIUM
THORIUM
YTTRIUM
ERBIUM
TERBIUM

CERIUM
LANTHANUM
DIDYMIUM

IRON
MANGANESE
ZINC
TIN
CADMIUM
COPPER
LEAD
BISMUTH
COBALT
NICKEL
CHROMIUM
VANADIUM
TUNGSTEN
COLUMBIUM

NIOBIUM
ILMENIUM
MOLYBDENUM
URANIUM
TELLURIUM
TITANIUM
ANTIMONY
ARSENIC

MERCURY
SILVER
GOLD
PLATINUM
PALLADIUM
RHODIUM
RUTHENIUM
OSMIUM
IRIDIUM

Two which are but imperfectly known—namely, NORIUM, and PELOPIUM—are excluded from this list. Altogether, the number of metals known is 52.

The first five of the metals upon the above list are distinguished as the metals of the alkalies; their oxides are powerfully alkaline; they have an intense affinity for oxygen, and decompose water at all temperatures. The next four metals are the bases of the alkaline earths; with the exception of magnesium, they also decompose water at all temperatures. The ten succeeding metals, with the exception of aluminum, have been but imperfectly examined; they are generally designated as the bases of the earths. The following twenty-two metals have been sometimes divided into those which form basic oxides, and those which form acids; and they have been separated into other distinctive groups, having reference to the action of acids upon them, to their action upon water at high temperatures, and to the isomorphism of their salts; these characters, however, are not sufficiently definite; and as regards the basic or the acid character of their compounds with oxygen, several of them form compounds belonging to both classes. The last nine metals have been particularly designated as noble metals; they are not changed by air or by water, and their affinity for oxygen is comparatively feeble: to some of these properties, however, osmium forms an exception.

Physical Properties.—A high degree of *lustre* is one of the leading physical characters of the metals, the color of the light which they reflect varying with the nature of the metal and the number of reflections to which it has been subjected. In most cases it is nearly white, gray, or bluish; from gold it is yellow, and from copper, red; but the intensities of these colors may be greatly increased by repeated reflections.

The *opacity* of metals is such, that when in very thin leaves they transmit no light. Gold is so far an exception, that when beaten into leaves of one two-hundred-thousandth of an inch in thickness it transmits green light, and if alloyed with silver, blue light. There are also other means by which extremely thin metallic films may be obtained, and which often exhibit a certain amount of transparency.

Hardness—Brittleness.—Few of the metals, when pure, are very hard; they are generally softer than steel. Lead may be scratched by the nail; and potassium at 60° is softer than wax. Some, such as antimony, arsenic, and bismuth, may be easily pulverized; others are brittle at one temperature, but malleable and ductile at another. Zinc, for instance, which at common temperatures is comparatively brittle, may be rolled and drawn into wire when heated up to 300°.

Malleability, or the capacity of being extended by hammering or rolling, belongs to some of the metals in a very remarkable degree. Common gold-leaf, for instance, is not more than a 200,000th of an inch in thickness; and 3 grains of the metal are sufficient to cover a square foot. Silver, copper, and tin, also admit of great extension under the hammer. In hammering and rolling, some of the metals become so hard and brittle as to require occasional annealing; in these cases they give out much heat. The following is the order of malleability—gold, silver, copper, aluminum, tin, cadmium, platinum, lead, zinc, and iron.

Ductility.—The malleable metals are also *ductile;* that is, they admit of drawing out into wire. In this respect, gold, silver, platinum, and iron, stand at the head of the list. A grain of gold may be drawn into 500 feet of wire. A wire of platinum, not exceeding a 30,000th of an inch diameter, has been obtained by placing it in the axis of a small cylinder of silver, and then drawing the compound wire in the usual way, and afterwards dissolving off the silver by nitric acid. The order of ductility is as follows: gold, silver, platinum, iron, copper, aluminum, zinc, tin, and lead.

Tenacity, or the power of supporting a weight without breaking, is an important property of the metals. Iron is at the head of the list, and lead at the bottom; but the respective tenacities are much influenced by the temperature at which the comparisons are made, the manner in which they are tested, and more especially by the process of annealing. A wire of unannealed iron, which sustained a weight of 26 lbs. only bore 12 lbs. after having been annealed; and a wire of copper which sustained 22 lbs. before annealing, was broken by 9 lbs. after annealing. The following metals are arranged in the order of their tenacities: iron, copper, palladium, platinum, silver, gold, zinc, tin, lead. The tenacity of iron compared with lead is as 25 to 1.

In the following table the figures represent the number of pounds required to break wires one-tenth of an inch in diameter:—

Lead	27·7	Zinc	100·8	Silver	187·1	Copper	302·2
Tin	34·7	Gold	150·7	Platinum	274·3	Iron	549·5

The tenacity of a metal, with few exceptions, decreases in proportion as its temperature increases; but iron, though less tenacious at 212° than at 32°, is more so at 890° than at 212°.

Crystallization.—Metals are susceptible of assuming the crystalline form. With many, this may be effected by fusion and slow cooling, and especially by suffering the melted metal to concrete externally, and then perforating the solid crust, and pouring out the liquid interior. The cavity so formed will be then lined with crystals: this mode of proceeding answers extremely well with bismuth, which furnishes a singular congeries of cubic crystals (page 25). When the metals are precipitated by each other, they often crystallize during their deposition, as in the precipitation of silver by mercury, and in that of lead by zinc. A stick of phosphorus immersed in a solution of silver becomes incrusted with metallic crystals (p. 221). Gold is occasionally deposited in a crystalline form, from its ethereal solution. During the electrolysis of metallic solutions, especially when low powers are employed, beautiful crystals are also occasionally obtained.

The crystalline structure of a metal materially affects some of its other physical properties. Copper, silver, and even gold, become comparatively hard and brittle when in a crystalline condition; and the most brittle metals are those which most readily assume the crystalline form, such as bismuth and antimony. Even iron, which in one condition is fibrous, tough, and tenacious, becomes relatively brittle, when it assumes even an approach to a crystalline structure; and this change in its condition is sometimes the result of changes of temperature, and shows itself in bars and axles which have been subjected to protracted friction and vibration.

Specific Gravity.—The specific gravities of the metals, or their relative densities, as compared with distilled water at the temperature of 60°, are shown in the following table; they include the lightest and the heaviest solids. The metal lithium is lighter than all known solids and liquids:—

Osmium	21·40	Cobalt	8·9	Arsenic	5·9
Platinum	21·15	Copper	8·9	Chromium	5·9
Iridium	21·15	Nickel	8·8	Titanium	5·3
Gold	19·3	Molybdenum	8·6	Aluminum	2·6
Tungsten	17·6	Cadmium	8·6	Strontium	2·5
Mercury	13·5	Manganese	8·0	Glucinum	2·1
Rhodium	12·0	Iron	7·8	Magnesium	1·7
Palladium	11·8	Tin	7·2	Calcium	1·5
Ruthenium	11·3	Zinc	7·1	Sodium	0·97
Lead	11·4	Columbium	6·9	Potassium	0·86
Silver	10·5	Antimony	6·7	Lithium	0·59
Bismuth	9·8	Tellurium	6·6		

[The reader is referred to the Appendix for the rules to be observed in taking the specific gravity of metals and other solids.]

RELATION OF METALS TO HEAT.—The changes of *bulk* which metals undergo with changes of *temperature* are relatively greater than those of other bodies, but each metal has its peculiar rate of expansion, as shown in the following table, in which 1,000,000 parts of each metal are supposed to be heated from 32° to 212°.

	Increase in length.	Increase in bulk.		Increase in length.	Increase in bulk.
Platinum	1 in 1131	1 in 377	Copper	1 in 582	1 in 194
Palladium	1 in 1000	1 in 333	Silver	1 in 524	1 in 175
Antimony	1 in 923	1 in 307	Tin	1 in 516	1 in 172
Iron	1 in 846	1 in 282	Lead	1 in 351	1 in 117
Bismuth	1 in 718	1 in 239	Zinc	1 in 340	1 in 113
Gold	1 in 682	1 in 227			

The expansion of glass is nearly the same as that of platinum, hence wires of that metal may be welded into fused glass without inconvenience, but if we substitute a wire of another metal, its different rate of contraction tends to break the glass as it cools. So also a compound bar of iron and copper, or of platinum and silver, formed by riveting strips of the metals to each other, though it remains straight at the temperature at which they were riveted, becomes warped or curved when heated or cooled. The metallic thermometer, and the compensation pendulum or balance-wheel as applied to clocks and watches, are illustrations of the same principle.

The *force* exerted in this act of metallic expansion is so considerable as often to produce injurious effects when not adequately provided for, as in railways, bridges, water and gaspipes, and in the beams, columns, and roofs of buildings.

The expansion of a metallic bar has been successfully applied as a means of measuring high temperatures, as in *Daniell's Pyrometer.*

That the metals are excellent *conductors of heat* is learned by the rapidity with which heat passes from one end to the other of a metallic bar; and that the different metals thus transmit heat with different degrees of facility, is shown by comparative experiments. If, for instance, two similar bars of silver and of platinum be heated at one end, the silver will be more rapidly heated throughout than the platinum. Gold, silver, and copper are among the best conductors; then come iron, zinc, and tin; and lastly, lead. A consequence of this property of the metals is, that they communicate and abstract heat more readily than other bodies; that they feel hotter and colder than wood, or other bad conductors, though of the same temperature. If the thermo-conducting power of gold be assumed as = 100, that of silver will be about 98, of copper 90, of iron, 38, of tin 30, and of lead only 18.

The *polished metals* are remarkable for their low power of emitting and of receiving *radiant heat.* A polished metallic vessel filled with hot water, is a long time in cooling; and such a vessel containing cold water, and placed before the fire, is a long time in acquiring heat. When the polish is taken off, the radiating and receptive powers of such vessels are increased; but under all circumstances the metals are bad radiators. If we compare the radiating power of a surface coated with lamp-black, with that of polished gold, silver, copper, or tin, it is nearly as 100 to 12; and all tarnished metals radiate better than those which are bright and clean.

Fusibility.—The metals are all susceptible of fusion by heat, but the temperatures at which they liquefy are extremely various. At higher temperatures than those required for their fusion, the metals are *volatile,* and many of them may be distilled in close vessels. Mercury is volatile at temperatures above 40°. A piece of gold leaf suspended over it in a stopped bottle becomes slowly whitened by amalgamation. Cadmium, potassium, sodium, tellurium, and zinc, are volatile at a red heat, and arsenic below a red heat. Gold and silver are converted into vapor when exposed to intense heat; and most of the other metals evaporate under similar circumstances.

Although the melting-points will be described under the heads of the respective metals, it will be convenient to give in this place a table showing how some of the more important metals differ from each other, in regard to the temperature at which they pass from the solid to the liquid state. The metals are here arranged in two groups: 1, those which are fusible *below* a red heat (1000°); and 2, those which are fusible *above* this temperature. The metals not included in this list can be readily fused only under the oxy-hydrogen blowpipe:—

FUSIBLE BELOW A RED HEAT.

Mercury	40°	Bismuth	500°
Potassium	150°	Lead	612°
Sodium	200°	Zinc	773°
Lithium	356°	Antimony	900°
Tin	442°	Calcium	1000°
Cadmium	442°	Magnesium	1000°

FUSIBLE ABOVE A RED HEAT.

Aluminum	1750°	Gold	2016°
Silver	1873°	Cast-iron	2786°
Copper	1996°		

Specific Heat of the Metals.—By the term *specific heat* is meant the quantity of heat required to raise similar quantities of different substances to the same temperature. If we thus compare *oil* and *water*, it will be found that the quantity of heat required to raise the temperature of a pound of oil from 32° to 212° is only half that which is required to produce the same change of temperature in water; hence the specific heat of water being = 1, that of oil is 0·5 (p. 128). If we thus compare water with *mercury* we find that the specific heat of water being = 1·000, that of an equal *weight* of mercury is only 0·033. The specific heat of water, therefore, or, in other words, its *capacity for heat*, is very great compared with that of the metals, as shown in the following table; from which it will also be seen that the specific heat of bodies increases with their temperatures, so that it requires more heat to raise them a given number of degrees when they are at a high than when at a low temperature. The specific heats are in all cases compared with water, as = 1:—

	Between 32° and 212°.	Between 32° and 572°.		Between 32° and 212°.	Between 32° and 212°.
Iron	0·1098	0·1218	Antimony	0·0507	0·0547
Zinc	0·0927	0·1015	Platinum	0·0335	0·0355
Copper	0·0949	0·1913	Mercury	0·0330	0·0350
Silver	0·0557	0·0611			

When the specific heat of the elementary bodies is multiplied into their atomic weights, the product is (with some exceptions) nearly the same (p. 65).

RELATION OF THE METALS TO ELECTRICITY AND MAGNETISM.

In respect to *electrical conduction*, silver is the best, and mercury the worst conductor. Assuming the electro-conduction of silver as=100, that of copper is about 92, gold 65, zinc 24, tin 14, iron 12, lead and platinum about 8, and mercury 2. These conducting powers are remarkably influenced, in some cases, by temperature. Thus, in reference to tin, if its conducting power at 32° be=16, at 212° it will only be=10; so that, in general, the lower the temperature of the metal, the higher its electro-conducting power. Metals which are bad conductors of electricity, become most heated by an electric current, as is well shown by transmitting a current of electricity through a wire composed of alternate lengths of platinum and silver; the platinum only becomes red-hot.

Magnetism.—The peculiarities of iron in respect to magnetism have been long known, as also its permanent retention by steel. When a bar of iron is suspended between the poles of a magnet, it is equally attracted by each, and places itself parallel to the magnetic axis. Some metals are similarly affected, though in an inferior degree; but there are others which appear to be repelled by the magnetic poles, and which, when properly suspended between them, assume a direction at right angles to the magnetic axis, placing themselves *equatorially.* Faraday, who first observed these phenomena, terms such substances *diamagnetics.* He has shown that various solids, liquids, and gases, include magnetic and diamagnetic substances (p. 78); and that, as far as the metals are concerned, they may be arranged in the following order:—

Magnetic.

Iron
Nickel
Cobalt
Manganese
Chromium
Cerium
Titanium
Palladium
Platinum
Osmium

Diamagnetic.

Bismuth
Antimony
Zinc
Tin
Cadmium
Sodium
Mercury
Lead
Silver
Copper
Gold
Arsenic
Uranium
Iridium
Tungsten

CHAPTER XXIII.

POTASSIUM (K=39).

POTASSIUM (Kalium) was discovered by Davy in 1807. He obtained it by submitting caustic potassa to the decomposing action of voltaic electricity: the metal was slowly evolved, together with hydrogen, at the negative pole. By this process, however, it could only be procured in small quantities, and other methods have since been devised: that which is now usually adopted consists in subjecting a mixture of carbonate of potassa and charcoal to a high temperature, in a wrought iron distillatory apparatus, to which a proper receiver is adapted. The potassium which first passes over requires to be purified by a second distillation, to free it from a quantity of black matter which is of an explosive nature, and consists of a compound of potassium with carbon and carbonic oxide. In these distillations, the contact of the metal with air must be carefully guarded against: for this purpose it is usually received into, and preserved under, naphtha, or some liquid hydrocarbon, upon which it has no action. In this process the carbon deprives the carbonate of potassa of its oxygen, forming carbonic oxide, which abundantly escapes during the distillation; and if such decomposition were entire, 69 parts of the carbonate should yield 39 parts of potassium. It would be as follows: $KO,CO_2+C_2=K+3CO$. But the actual product of potassium falls far short of this result; and in consequence of some of the potassa escaping decomposition, and of the formation of carbide and oxicarbide of potassium, not more than one-fourth of the potassium contained in the mixture subjected to distillation, is usually obtained.

Potassium is a bluish-white metal of great lustre. It instantly tarnishes by exposure to air, and is gradually converted into an oxide. At 60° it is of the consistency of soft wax. Its sp. gr. is 0·86. It is most conveniently preserved in naphtha, in a well-stopped phial. It fuses at 150°; and at a bright red heat, in close vessels, it boils, and rises in green vapor. At 32° it is brittle, and of a crystallized structure. If heated in air, it burns with a brilliant flame. It is a good conductor of electricity and heat, and its lustre is well shown by fusing it under naphtha, through which it is seen as brilliant as mercury; or by flatting a clean slice of it by pressure between two pieces of plate glass.

POTASSIUM AND OXYGEN.—There are three oxides of potassium, namely, a *suboxide*=K_2O, a *protoxide*=KO, which in the state of *hydrate* constitutes *caustic potassa*=KO,HO, and a *peroxide*=KO_3.

SUBOXIDE OF POTASSIUM (K_2O) is formed by heating potassium in a limited portion of air, or by heating 1 part of potassium with $1\frac{1}{5}$ of hydrate of potassa; while hot it is reddish, but gray when cold: it is fusible and inflammable, taking fire when gently heated. Water converts it, without combustion, into potassa, hydrogen being evolved.

PROTOXIDE OF POTASSIUM. ANHYDROUS POTASSA (KO) is most readily obtained by heating 1 atom of potassium, $=39$ with one of hydrate of potassa $=56$: hydrogen is evolved, and 2 atoms of protoxide are formed ($K+KO, HO=2KO+H$). When 1 atom of potassium acts upon 1 atom of water out of the contact of air, it is also produced ($K+HO=KO+H$). When peroxide of potassium is intensely heated, it loses oxygen and leaves protoxide. It is a hard gray brittle substance, fusible at a bright red heat, sp. gr. about 2·65 ; extremely caustic and alkaline.

The composition of this oxide is learned by the action of potassium upon water; when the metal is thrown upon water, or even upon ice, it inflames, with the evolution of hydrogen, and burns with a violet-colored flame, producing a small globule of fused potassa, which, in combining with water, produces so much heat as to cause a slight explosion. If the potassium be plunged under water the decomposition ensues with explosive violence, but by carefully employing small quantities of the metal, or by previously amalgamating it with mercury, the experiment may be so conducted as to collect the evolved hydrogen, which thus becomes the indicator of the quantity of oxygen taken by the potassium, 100 parts of which are thus found to combine with 20·51 of oxygen: and 20·51 : 100 : : 8 : 39 ; so that the equivalent of potassium thus deduced is 39.

HYDRATED PROTOXIDE OF POTASSIUM; CAUSTIC POTASSA (KO,HO) is procured by decomposing carbonate of potassa by lime. The process consists in boiling in a clean iron vessel pure carbonate of potassa, with half its weight of pure quicklime, in not less than 7 or 8 parts of water. The lime, previously slaked, is gradually added to the boiling alkaline solution, which is kept constantly stirred, and towards the end of the operation it is tested by filtering a small portion, and pouring it into three or four times its bulk of dilute nitric acid; if there be no effervescence, sufficient lime has been used; but if carbonic acid escapes, the ebullition with lime must be continued, taking care to keep up the original quantity of water, until the tested portion shows no signs of carbonic acid. The whole is then allowed to remain quiet, that the carbonate of lime and excess of the hydrate of lime may subside; the clear liquor, or *lye*, may then be siphoned or poured off, concentrated by evaporation, strained through a clean calico filter, and set by in a well-stopped bottle till it admits of being decanted from any sediment. When the lye is evaporated in a polished iron or pure silver vessel, it assumes the appearance of an oily liquid, and concretes on cooling. When cast into sticks it is employed in surgery as a powerful and rapidly-acting caustic: in this state it generally contains some peroxide and other impurities, and evolves oxygen and deposits a sediment when dissolved in water. It is sometimes further purified by boiling it in a silver basin with highly-rectified alcohol for a few minutes, and then setting it by in a stopped phial; when the impurities are deposited, the alcoholic solution may be poured off and rapidly evaporated to dryness in a silver vessel; or if the quantity of alcohol be considerable, it may be distilled off in a silver alembic with a glass head: the heat may then be raised so as to fuse the potassa, which on cooling should be broken up and preserved in well-closed phials; if, however, pure materials and due care be employed, the alcoholic purification may be dispensed with, for even when so prepared the product contains traces of carbonate, and sometimes of acetate of potassa.

The pure hydrated oxide is white and somewhat crystalline in texture: its sp. gr. 2·1. It is fusible at a heat below redness, and evaporates from an open vessel, at a bright-red heat, in the form of acrid fumes. A platinum wire, dipped into potassa and heated by the blowpipe, communicates a characteristic violet tint to the flame. At a white heat it is decomposed by charcoal, and carburetted hydrogen, carbonic oxide, and potassium, are the products. It quickly absorbs moisture and carbonic acid from the air, and is soluble in half its weight of cold water. When reduced to a powder and slightly moistened it forms a crystallized combination which is a *terhydrate* (KO,3HO). By keeping a strong aqueous solution of potassa at a low temperature in a stopped phial, crystals may be obtained which are a *pentahydrate* (KO,5HO).

Caustic potassa is highly alkaline, reddening turmeric, and changing several vegetable blues to green. It acts energetically upon the greater number of organic products, and saponifies the fat oils. When touched with moist fingers it has a soapy feel, in consequence of its action upon the cuticle, and it then exhales a peculiar odor: this is also perceptible in the solution of potassa, and is probably referable to the formation of ammonia, arising from traces of organic matter accidentally present. In the fused state, it produces heat when dissolved in water; but in its crystallized state it excites considerable cold, especially when mixed with snow. It dissolves sulphur and several sulphides, and silica and alumina. The oxides of several of the other metals are also soluble in an aqueous solution of potassa.

When a solution of caustic potassa is required to be filtered, it is apt to act upon the filter and to absorb carbonic acid, so that filtration should as far as possible be avoided, and the liquor obtained clear by subsidence. On the large scale, linen strainers are generally used; upon the small scale, the absorption of carbonic acid may be prevented, by covering the funnel with a plate of glass, and receiving it into a bottle as nearly air-tight as possible.

A solution of potassa acts gradually upon flint glass, which contains oxide of lead; hence green glass vessels are preferable; but when the alkaline solution is to be exposed to heat, or evaporated to dryness, even these communicate impurity, and in such cases vessels of pure silver must be used, for almost all other metals, platinum not excepted, are more or less acted upon.

The solution of caustic potassa is frequently impure from the presence of carbonic acid, silica, alumina, lime, oxide of lead, and sulphuric or hydrochloric acid. If nitric acid cause an effervescence when dropped into it, it indicates *carbonic acid ;* if a gelatinous precipitate, not soluble in very slight excess of acid, it is *silica ;* if soluble, it is *alumina.* The presence of *lime* is shown by adding oxalate of ammonia to the solution previously neutralized by nitric acid ; in the same solution nitrate of silver will indicate hydrochloric acid, or *chlorine,* and nitrate of baryta, *sulphuric acid,* or *sulphates.* Freedom from metallic impurities is shown by hydrosulphate of ammonia, which should occasion no precipitate or change of color.

The following table shows the quantity of anhydrous potassa contained in aqueous solutions of different specific gravities. The boiling point of a saturated solution, sp. gr. 1·68, is 329°; of the officinal solution, sp. gr. 1·06, 213°.

Specific gravity.	Potassa per cent.	Specific gravity.	Potassa per cent.	Specific gravity.	Potassa per cent.	Specific gravity.	Potassa per cent.
1·68	51·2	1·44	36·8	1·33	26·3	1·15	13·
1·60	46·7	1·42	34·4	1·28	23·4	1·11	9·5
1·52	42·9	1·39	32·4	1·23	19·5	1·06	4·7
1·47	39·6	1·36	29·4	1·19	16·2		

PEROXIDE OF POTASSIUM (KO_3) is formed when potassium is burned with free access of air, or in oxygen gas; it is a yellow fusible substance, which, on cooling, acquires a crystalline appearance. It has some singular properties; it supports the combustion of most of the inflammables, and when heated in hydrogen, diminishes the bulk of the gas, and forms water; it decomposes ammonia under the same circumstances. When put into water, oxygen is evolved, and a solution of potassa obtained. When hydrated potassa is fused in an open crucible, a portion of its water is disengaged, and oxygen absorbed, so as to form this peroxide; hence it is that common caustic potassa almost always gives out oxygen when put in water.

POTASSIUM AND CHLORINE; CHLORIDE OF POTASSIUM (KCl).—Potassium burns brilliantly in chlorine, especially if introduced into the gas in the state of fusion, as, otherwise, a crust of chloride is apt to form and protect the interior from further action.

When potassium is heated in gaseous hydrochloric acid, chloride of potassium is formed, and hydrogen evolved: $K+HCl=KCl+H$. It is also formed by dissolving potassa or its carbonate in hydrochloric acid, and evaporating to dryness. The affinity of potassium for chloride exceeds that for oxygen; so that potassa heated in chlorine, loses oxygen, and yields chloride of potassium: hence, also, potassium heated with other chlorides, evolves their bases and forms chloride of potassium. When chlorine is passed over iodide of potassium at a red heat, iodine is expelled, and chloride of potassium formed.

Chloride of potassium dissolves in three parts of water at 60°. One part of the powdered salt stirred into four parts of cold water, produces a depression of temperature of between 20° and 25°, whereas chloride of sodium under the same circumstances only depresses the thermometer between 2° and 3°: hence it has been proposed to estimate the relative proportions of these chlorides when mixed, by the depression of temperature resulting from their solution. Chloride of potassium crystallizes in cubes; its taste is saline and bitter. Its sp. gr. is 1·9. In old pharmacy it was called *digestive salt of Sylvius;* also, *regenerated sea-salt.* It is insoluble in alcohol. When intensely heated in open vessels, it evaporates in the form of white fumes. This salt is a residue of several chemical and pharmaceutical processes, and is sometimes found in rough saltpetre; it is also contained in kelp, and in the juices of many plants. The crystals, which occur in old pharmaceutical extracts, are usually of this salt. The manufacturers of alum occasionally employ it as the source of potassa in that salt.

HYPOCHLORITE OF POTASSA (KO,ClO), called also *chloride of potassa,* and *chlorinated potassa* has only been obtained in solution by adding aqueous hypochlorous acid to a solution of potassa. When chlorine is passed into a solution of carbonate of potassa so as not quite to saturate the alkali, carbonic acid is evolved, and a solution of hypochlorite of potassa is obtained, provided the liquor be kept cold. If heated, or if more than one atom of chlorine to one of potassa be used, the hypochlorite is decomposed, and part of the bleaching power of the solution destroyed. A solution of hypochlorite of potassa is also obtained by double decomposition, when solution of hypochlorite of lime is mixed with carbonate of potassa. It is colorless, powerfully bleaching, and antiseptic. When chlorine is passed over slightly moistened carbonate of potassa, a bleaching salt mixed with bicarbonate is the result.

CHLORATE OF POTASSA (KO,ClO_5) is formed by passing excess of chlorine through a strong solution of potassa: chloride of potassium is one of the results, the other is *chlorate of potassa*, a salt in brilliant rhomboidal tables, (formerly called *oxymuriate of potassa*). By concentrating the liquid, the chlorate of potassa, which is much less soluble in cold water than the chloride of potassium, is deposited on cooling.

The action of chlorine upon a solution of *carbonate of potassa* at first produces bicarbonate of potassa, which, by the continued action of chlorine, is decomposed, the whole of the carbonic acid expelled, and *hypochlorite of potassa* and *chloride of potassium* are then formed; $6KO+6Cl=3KCl+3[KO,ClO]$: the hypochlorite is itself afterwards resolved into chlorate and chloride; $3[KO,ClO]=KO,ClO_5+2KCl$: so that the ultimate result may be thus represented: $6KO+6Cl=5KCl+KO,ClO_5$.

The following is the most economical process for the preparation of this chlorate. One equivalent of carbonate of potassa and one of hydrate of lime are mixed and exposed to a current of chlorine; the mass becomes hot, and evolves water during the absorption of the gas: when saturated, it is gently heated to complete the decomposition. No oxygen is evolved, the action being such that $6[KO,CO_2]$, and $6[CaO,HO]$, acted on by 6Cl, yield $5KCl+6[CaO,CO_2]+KO,ClO_5$; whilst 6HO are evolved. By the action of water, the soluble salts are separated from the carbonate of lime, and the chloride and chlorate by crystallization.

Chlorate of potassa is an anhydrous salt of a cooling taste. It forms tabular crystals of a pearly lustre. Its specific gravity is 1·9. When pure, its aqueous solution is not rendered turbid by nitrate of silver. When triturated, it appears phosphorescent. It decrepitates and fuses at a temperature between 400° and 500°: at a higher heat it effervesces, and gives out nearly 40 *per cent.* of oxgen, and chloride of potassium remains (*see* p. 82). It is soluble in 18 parts of cold, and in 2·5 of boiling water; and in about 120 parts of alcohol. Its acts energetically upon many inflammables, and when triturated with sulphur, phosphorus, and charcoal, produces inflammation and explosion. A mixture of three parts of this chlorate with one of sulphur, detonates loudly when struck with a hammer, and even sometimes explodes spontaneously. When sulphuric acid is dropped upon mixtures of this salt and combustibles, ignition ensues, in consequence of the evolution of peroxide of chlorine. A mixture of sugar and the chlorate thus treated, is immediately kindled; and a mixture of sulphide of antimony and the salt, suddenly deflagrates with a bright puff of flame and smoke; the latter mixture requires to be cautiously made, as it often takes fire by gentle trituration.

PERCHLORATE OF POTASSA; OXYCHLORATE OF POTASSA (KO, ClO_7).—This salt is formed when chlorate of potassa is heated in a porcelain crucible till it fuses, and by giving out a portion of oxygen, becomes thick and pasty; the cooled mass, dissolved in hot water, deposits perchlorate of potassa on cooling, which may be purified by recrystallization. The chloride of potassium and undecomposed chlorate remain in solution. The action of heat on 2 equivalents of the chlorate forms one of chloride of potassium, and 1 of perchlorate; while 4 of oxygen are evolved: $2(KO,ClO_5)=KCl+KO,ClO_7+O_4$. This salt forms anhydrous rhombic crystals, soluble in 65 parts of water at 60; at a high temperature it is resolved into oxygen and chloride of potassium.

IODIDE OF POTASSIUM (KI).—Iodine and potassium act upon each other very energetically, and often with explosion, and a crystalline compound is obtained, white and fusible. When hydriodic acid is saturated with potassa, and the solution carefully evaporated, anhydrous crystals of the iodide are obtained. The usual mode of procuring this compound consists in dissolving iodine in solution of potassa till it begins to assume a brown color; on evaporating to dryness, and fusing the residuary salt at a red heat, iodide of potassium remains, generally mixed, however, with a little iodate; if a little charcoal is added previous to fusion, the decomposition is complete. If, instead of fusing the products, the solution be evaporated nearly to dryness, and alcohol poured upon it, the iodide is dissolved, and *iodate of potassa* remains, which, at a red heat, evolves oxygen, and becomes iodide of potassium. The action of iodine upon the alkali corresponds with that of chlorine; that is 6KO, and 6I, produce 5KI, and KO,IO_5; and then, by the application of heat, KO,IO_5 becomes KI, and 6O are given off. Iodide of potassium is also prepared by decomposing a solution of iodide of iron or of zinc, by carbonate of potassa, and filtering and evaporating the resulting solution; $FeI+KO,CO_2$ become KI, and FeO,CO_2.

Iodide of potassium forms cubic crystals, of an acrid saline taste; they are anhydrous, and slightly deliquescent in damp air. 100 parts of water at 65° dissolve 143 of this salt, and a considerable depression of temperature is produced during the solution. It should be purchased in crystals, which ought not to be very deliquescent, and should dissolve in six or eight parts of alcohol, sp. gr. ·836. They generally redden turmeric, from the presence of a little carbonate of potassa. The usual impurities in the iodide, are chloride of potassium and sodium, iodate of potassa, and water. To detect chlorine, the iodide may be decomposed by nitrate of silver, and the washed precipitate digested in strong solution of ammonia; if the filtered solution, acidified by nitric acid, gives a white precipitate, it is chloride of silver. To detect iodate of potassa, add to the solution of iodide, a solution of tartaric acid. If a yellow or brown color is produced, this indicates the presence of iodate. When starch is added, the liquid acquires a deep blue color. The aqueous solution of iodide of potassium dissolves a considerable portion of iodine; this solution, under the name of *ioduretted iodide of potassium*, is sometimes used in medicine. Iodide of potassium is decomposed by chlorine, and even when largely diluted, a minute quantity of chlorine discolors the solution; sulphuric or nitric acid (containing nitrous acid) also decomposes it. Chloride of platinum reddens a solution containing only a 12,000th of the iodide; and protonitrate of mercury produces a yellow cloud, where only a 60,000th is present. Paper which has been bleached by chlorine is generally discolored by iodide of potassium; and if characters are written or figures drawn with a solution of iodide of potassium, they are rendered visible, in the manner of sympathetic ink, by the slightest breath of chlorine. When paper imbued with a mixed solution of starch and iodide of potassium is exposed to the air in certain situations, it sometimes becomes more or less discolored in consequence of the presence of ozone (p. 104); there are other causes, however, which may occasionally produce this change.

IODATE OF POTASSA (KO,IO_5) is, as above stated, one of the products of the action of iodine on a solution of potassa; after evaporation the iodide of potassium may be separated from the iodate by digestion in alcohol sp. gr. 810, which leaves the latter salt undissolved. Iodate of potassa requires about 14 parts of water at 60° for its solution; it is insoluble in absolute alcohol. Its crystals are small cubes, permanent in the air; at a red heat it gives out between 22 and 23 per cent. of oxygen, and is converted into iodide of potassium, no periodate being intermediately formed. Its aqueous solution is decomposed by sulphuretted hydrogen, and by sulphurous and arsenious acids.

BROMIDE OF POTASSIUM (KBr).—Potassium and bromine act intensely upon each other, evolving heat and light, and producing explosion. When bromine is dropped into solution of potassa, the mixture evaporated, and the residue heated to redness, *bromide of potassium* is also obtained. Its sp. gr. is 2·4; it is white, fusible, and crystallizes in cubes, easily soluble in water, and slightly so in alcohol. It is prepared for medical use, by decomposing bromide of zinc or bromide of iron, by carbonate of potassa; it should be purchased in crystals, as it is otherwise apt to be impure.

NITRATE OF POTASSA; NITRE; SALTPETRE (KO,NO_5).—This salt is principally brought to this country from the East Indies, where it is produced by lixiviation from certain soils; but the mode or cause of its formation is not well understood; it is probably connected with the oxidation of ammonia. The greater part of the rough nitre imported from the East Indies is in broken down crystals, which are more or less deliquescent; exclusive of other impurities, it often contains a considerable portion of common salt, which, reacting upon the nitre, sometimes induces the production of nitrate of soda and chloride of potassium; it also usually contains sulphate of lime and traces of organic matter. In Germany and France, it is artificially produced in what are termed nitre-beds. The process consists in lixiviating old plaster rubbish, which, when rich in nitre, affords about five per cent. Refuse animal and vegetable matter, which has putrefied in contact with calcareous soils, produces nitrate of lime, which affords nitre by mixture with carbonate of potassa.

The loss which rough nitre sustains in refining is technically termed the *refraction*, and can only be ascertained by analysis, which frequently is somewhat intricate.

Nitre crystallizes in anhydrous, six-sided prisms, usually terminated by dihedral summits. Its sp. gr. is about 2. The solubility of nitre varies extremely with temperature: at 32°, 100 parts of water dissolve 13·2 of the salt; at 77°, 38 parts; at 132°, 97 parts; at 176°, 169 parts; and at 212°, 246 parts. During the solution of 1 part of powdered nitre in 5 of water, the temperature sinks from 50° to 35°. It is insoluble in pure alcohol. The crystals of nitre, though the salt is anhydrous, generally contain interstitial water; so that they appear moist when powdered, and lose weight on drying. The taste of nitre is cooling and peculiar.

At a temperature of about 600°, nitre fuses without undergoing change of composition, and congeals on cooling. Sometimes it is cast into small balls or cakes, called *sal prunella*. At a red heat, nitre is slowly decomposed; and highly heated in an earthen retort, or gun-barrel, it affords oxygen gas, mixed with a portion of nitrogen. In this decomposition, the nitre is first converted into *hyponitrite of potassa*, which is somewhat deliquescent; potassa is the final result.

Nitre is rapidly decomposed by charcoal at a red heat, and the results are carbonic oxide and acid, nitrogen, and carbonate of potassa, formerly called *nitrum fixum*, and *white flux*. These mixtures of nitre and charcoal form the basis of a variety of compositions used for fireworks, the rapidity of the combustion being modified by the relative proportion of the charcoal. When phosphorus is thrown upon nitre, and inflamed, a vivid combustion ensues, and a phosphate of potassa is formed. Sulphur sprinkled upon hot nitre burns, and produces a mixture of sulphate and sulphite of potassa, formerly employed in medicine under the name of *polychrest salt*. Many of the metals, when in filings or powder, deflagrate and burn when thrown on red-hot nitre. A mixture of 3 parts of nitre, 2 of dry carbonate of potassa, and 1 of sulphur, forms *fulminating powder*. If a little of this is heated to about 330°, it blackens, fuses, and explodes with violence, in consequence of the rapid action of the sulphur upon the nitre, and the sudden evolution of nitrogen and carbonic acid, the residue being chiefly sulphate of potassa, $3[KO,NO_5]+2[KO,CO_2]+5S=5[KO,SO_3]+3N+2CO_2$. The action of sulphuric acid on nitre has been already described (p. 161). When nitre and hydrochloric acid are heated together, chlorine and nitrous acid are evolved, and on evaporation to dryness, chloride of potassium remains.

GUNPOWDER consists of a mixture of nitre, sulphur, and charcoal, the proportions varying according to the uses made of it, as follows:—

	Common gunpowder.	Shooting powder.	Shooting powder.	Miners' powder.
Saltpetre	75·0	78	76	65
Charcoal	12·5	12	15	15
Sulphur	12·5	10	9	20

The explosive force of gunpowder depends upon the sudden formation of nitrogen and carbonic acid gases, which, at the high temperature at which they are evolved, may be considered as amounting to about 1500 times the volume of the powder employed. Supposing the combustion perfect, and the powder to consist of:—

		Per cent.
1 equivalent of nitre	101	75·0
1 " sulphur	16	11·8
3 " carbon	18	13·2
	135	100·0

the resulting products may be thus represented: $KO,NO_5+S+C_3=3CO_2+N+KS$, the only residue being sulphide of potassium, which gives the fetid odor to the washings of a gun-barrel.

In the manufacture of gunpowder, the nitre and sulphur must be pure, the charcoal carefully selected and prepared, and the whole perfectly mixed in fine powder. This mixture is moistened, ground and pressed into a cake; it is then granulated, dried, and polished by attrition in revolving barrels. The granular form of the powder increases the rapidity of its combustion, by enabling the flame so to penetrate it as to kindle every grain nearly at the same time; but this combustion, though very rapid, is by no means instantaneous, for in that case scarcely anything would resist its power, and its explosion would more resemble that of fulminating mercury or silver, and would burst the gun instead of propelling the ball. A cubic foot of good gunpowder should weigh about 58 pounds; and 2 ounces of it, when exploded in a mortar 8 inches in diameter, and placed at an angle of 45°, should throw a 68 lb. shot about 270 feet.

Gunpowder is sometimes tried by placing two heaps of about sixty grains each upon clean writing paper, three or four inches asunder, and firing one of them by a red-hot wire; if the flame ascends quickly with a good report, sending up a ring of white smoke, leaving the paper free from specks and not burnt into holes, and if no sparks fly from it so as to set fire to the contiguous heap, the powder is good.

Analysis of Gunpowder.—Weigh off 100 grains reduced to fine powder, and dry it at 212° to estimate the moisture; then wash it upon a filter with boiling water, which dissolves out the whole of the nitre; dry the washed residue, and digest it in bisulphide of carbon, which abstracts the sulphur and leaves the charcoal. The aqueous solution, if the nitre be pure, should not be affected by nitrate of silver or nitrate of baryta.

ACTION OF POTASSIUM ON AMMONIA; POTASSIAMIDE.—When potassium is heated in gaseous ammonia, hydrogen is evolved, and an olive-colored substance is obtained, of a crystalline fracture. It burns in oxygen, producing hydrated potassa, and nitrogen; exposed to air, it deliquesces, and evolves ammonia; water acts upon it, producing potassa and ammonia. The volume of hydrogen evolved by this action of potassium on ammonia, is the same as that which it would have evolved from water; so that when 1 atom of potassium acts upon 1 of ammonia, 1 of hydrogen is evolved, and the remaining elements of the ammonia (namely, 1 atom of nitrogen and 2 of hydrogen) combine with the potassium; now 1 of nitrogen and 2 of hydrogen constitute *amidogen*, hence this resulting compound has been termed *potassiamide*, its formula being K,NH_2; an atom of the hydrogen of the ammonia being replaced by an atom of potassium (*see* page 169). Heated in hydrogen, potassium absorbs a portion of that gas, and forms a gray *hydride*, which is very inflammable : it is decomposed by the contact of mercury ; it is said to consist of 1 atom of hydrogen combined with 4 of potassium.

SULPHIDES OF POTASSIUM.—When sulphur and potassium are heated in an exhausted tube, vivid combustion ensues, and if atomic proportions be observed, a *protosulphide of potassium* is formed$=KS$. So also when a stream of hydrogen is passed over heated sulphate of potassa, water and the protosulphide are the results: ($KO,SO_3+4H=KS+4HO$). If a mixture of 2 parts of sulphate of potassa and 1 of lamp-black is heated out of the contact of air, a *pyrophorus* is formed, which is a mixture of the protosulphide and charcoal. A solution of this protosulphide is obtained by dividing a solution of caustic potassa into two equal parts, and saturating one of them with sulphuretted hydrogen, by which the compound KS,HS is formed, and which, when mixed with the other half of the solution, is converted into protosulphide: $KS,HS,+KO=2KS+HO$. When this solution is evaporated, it yields a nearly colorless crystalline product, acrid and alkaline, and evolving sulphuretted hydrogen when an acid is added: thus (with sulphuric acid) $KS+SO_3HO=KO,SO_3+HS$. It absorbs oxygen when exposed to air, and becomes yellow.

Bisulphide of Potassium (KS_2) is formed by heating four parts of potassium with three of sulphur; or by exposing an alcoholic solution of KS,HS to the air, till it begins to deposit sulphur, and then evaporating *in vacuo ;* it is an orange-colored fusible substance.

Tersulphide of Potassium (KS_3) is formed by passing the vapor of bisulphide of carbon over carbonate of potassa at a red heat; carbonic oxide and carbonic acid are evolved; $2(KO,CO_2)+3CS_2=CO_2+4CO,+2KS_3$. The substance formerly known under the name of *Liver of Sulphur*, is a mixture of this tersulphide with sulphate of potassa; it is obtained by heating 70 parts of carbonate of potassa with 40 of sulphur; carbonic acid is evolved and $3KS_3+KO,SO_3$ is produced.

Tetrasulphide of Potassium (KS_4) is formed by passing the vapor of sulphide of carbon over heated sulphate of potassa.

Pentasulphide of Potassium (KS_5) is formed when solutions of the preceding sulphides are boiled with excess of sulphur; or when a solution of caustic potassa and excess of sulphur are boiled together. In this case, 3 equivalents of potassa and 12 of sulphur, yield 2 equivalents of the pentasulphide and 1 of hyposulphite of potassa; $3KO+12S=2KS_5+KO,S_2O_2$.

SULPHITE OF POTASSA (KO,SO_2) is formed by passing excess of sulphurous acid into a solution of potassa, and evaporating out of contact with air. Its crystals contain an atom of water.

SULPHATE OF POTASSA (KO,SO_3).—This salt is the result of several chemical operations carried on upon a large scale in the processes of the arts. It is the *sal de duobus* and *arcanum duplicatum* of the old chemists. Its taste is bitter and saline. It crystallizes in short six-sided prisms, terminated by six-sided pyramids. They are anhydrous, and soluble in about 12 parts of water at 60°, and insoluble in alcohol. This salt is thrown down when sulphuric acid is added to a moderately strong solution of potassa.

When about 2 parts of sulphate of potassa and 1 of lamp-black, intimately mixed in fine powder, are heated to redness in a coated phial, and great care taken to exclude the air during cooling, the product takes fire on exposure to air. It appears to contain a compound of potassium, which powerfully attracts oxygen, and thus evolves heat enough to inflame the charcoal and sulphur.

BISULPHATE OF POTASSA ($KO,HO,2SO_3$) is formed by heating in a platinum crucible 87 parts of sulphate of potassa with 49 of sulphuric acid. When one atom of sulphate is dissolved in from 3 to 5 atoms of oil of vitriol, and evaporated to crystallization, an anhydrous bisulphate first forms in acicular crystals, but in a few days it liquefies and is converted into rhomboidal hydrated crystals. This salt is not decomposed below redness; at a red heat it gives out sulphuric acid, sulphurous acid, and oxygen, and is converted into the neutral salt. It is soluble without decomposition in about half it's weight of boiling water, but by large quantities of water is resolved into neutral sulphate and acid. Bisulphate of potassa is also formed by the distillation of 1 atom of nitre and 2 of sulphuric acid, as in the process for obtaining *Nitric Acid* (p. 161); and, under the old name of *sal enixum*, it is used for cleansing metals.

PHOSPHIDE OF POTASSIUM (KP) is a chocolate-brown compound which rapidly decomposes water, evolving phosphuretted hydrogen gas. It is formed by cautiously heating atomic equivalents of potassium and phosphorus out of the contact of air.

CARBONATE OF POTASSA (KO,CO_2) is a salt of much importance, and known in different states of purity under the names of *wood-ash*, *pot-ash*, *pearl-ash*, *subcarbonate of potassa:* it was formerly known by other names, having reference to its sources; as *fixed nitre*, *salt of tartar*, *salt of wormwood*, *vegetable alkali*, *&c.* It may be obtained directly, by passing carbonic acid into a solution of potassa, till saturated, evaporating to dryness, and exposing the dry mass to a red heat; or indirectly, by burning purified *tartar* (bitartrate of potassa), lixiviating the residue, and evaporating to dryness. A mixture of purified tartar and nitre projected into a crucible heated to dull redness, also affords carbonate of potassa, which may be obtained by lixiviation as the preceding (*fixed nitre*). When succulent vegetables are burned, their potassa-salts are for the most part converted into carbonate, hence the term *vegetable alkali;* and particular plants afford it in larger quantities than others, especially *wormwood.* The younger branches of trees afford more than the old wood, hence their selection as a source of *wood-ash.*

Carbonate of potassa is generally derived from two sources, namely, from the carbonate of commerce, or from the bicarbonate. The carbonate of potassa of commerce is purified by lixiviating it with its weight of cold water; being more soluble than the salts which usually accompany it, these remain undissolved, and the solution, poured off, strained or filtered if necessary, and evaporated, leaves the carbonate of potassa. Or the crude carbonate may be dissolved in water, filtered, evaporated till the solution acquires the sp. gr. 1·52, and set aside in a cold place, when the greater part of the foreign salts are deposited, and the solution of the carbonate may be poured off; with every precaution, however, when thus obtained, it is still impure. When required pure, it is obtained by heating the *crystallized bicarbonate* to a temperature below redness, but sufficient to expel its water and half of its carbonic acid. When equal parts of bitartrate and nitrate of potassa are burned in successive portions in an iron crucible, the residuary carbonate was formerly called *white flux:* when 2 parts of tartar are used to 1 of nitre, the whole of the charcoal is not consumed, and the product was called *black flux;* these compounds being used in fusing or fluxing metallic ores.

Carbonate of potassa is fusible without decomposition, at a red-heat; its sp. gr. is 2·24: it is very soluble in water, which at 55° takes up nearly its own weight. It deliquesces by exposure to air, forming a dense solution, formerly called *oil of tartar per deliquium.* Its taste is alkaline, and it has a strong alkaline action upon test-papers. It is insoluble in alcohol. A saturated solution of carbonate of potassa in water contains about 48 per cent. of the salt, and has a sp. gr. of 1·5. When this solution is evaporated till its sp. gr. becomes 1·62, it yields deliquescent crystals which include 2 atoms of water. The solution will commonly be found to contain traces of sulphate and chloride, as well as oxide of lead dissolved from the glass. These impurities may be detected by their appropriate tests. As carbonate of potassa is usually derived from the ashes of vegetables, its production is limited to countries which require clearing of timber, or where there are vast natural forests. If vegetables growing in a soil not impregnated with sea-salt are burned, the residue, which is in the form of a brown saline mass, contains a large relative proportion of this carbonate, and is commonly called *rough,* or *crude potassa.* If it be again calcined so as to burn away the carbonaceous matter, it becomes a white mass, generally termed *pearlash.*

The pearlash of commerce contains a variety of impurities, which render it of variable value. In general, its purity may be judged of by its easy solubility in cold water, 2 parts of which should entirely dissolve 1 part of the salt; the residue consists of impurities. The quantity of acid of a given strength, requisite to saturate a given weight, may also be resorted to as a criterion of its purity. Now 355 grains of diluted sulphuric acid of the specific gravity of 1·141 neutralize 100 grains of pure carbonate of potassa. Hence, if we dissolve 100 grains of the alkali to be examined, in six or eight parts of water, and gradually add the test sulphuric acid till we find, by the application of proper test-papers, that the alkali is exactly neutralized, we may deduce, from the weight of the acid consumed, the proportion of real carbonate present: for as 355 is to 100, so is the weight of the test-acid employed, to that of the pure carbonated alkali present. To save trouble, the acid properly diluted may be put into a glass tube so graduated as to show directly the value of the alkali by the quantity consumed in its saturation. Thus we find, by reference to the scale of equivalents, that 100 parts of carbonate of potassa are saturated by 70 of sulphuric acid, specific gravity 1·84. If, therefore, we put 70 grains of such acid into a tube divided into 100 parts, and fill it up with water, it follows that the quantity of carbonate of potassa existing in any sample of pearlash under examination, will be directly shown by the measure of such diluted acid required for saturation; 100 grains of the sample, if pure carbonate, would require the whole 100 measures of acid; but if only containing 50 *per cent.* of pure carbonate, the 100 grains would be saturated by 50 measures of the test-acid, and so on. Such graduated tubes are sometimes called *alkalimeters,* and are to be obtained from the makers of chemical apparatus, together with practical directions for using them.

BICARBONATE OF POTASH ($KO,HO,2CO_2$) is formed by passing carbonic acid into a solution of the carbonate, or by subjecting the moist carbonate to excess of gaseous carbonic acid. It may also be obtained by the action of sesquicarbonate of ammonia on carbonate of potassa, in which case pure ammonia is evolved. Bicarbonate of potassa forms hydrated prismatic crystals, which are not deliquescent, and taste slightly alkaline. They require for solution about four parts of water at 60°. Boiling water dissolves nearly its own weight, but during the solution a portion of carbonic acid is evolved, and by long boiling, the salt is said to become a sesquicarbonate, or even carbonate. The solution has an alkaline reaction, and possesses most of the chemical properties of the carbonate. It is distinguished from the carbonate—1, in giving no precipitate in the cold, with a solution of sulphate of magnesia: and 2, in producing a pale yellowish precipitate with a few drops of a solution of corrosive sublimate. A solution of the carbonate gives *immediately* a brick-red precipitate of oxychloride of mercury. Bicarbonate of potassa is nearly insoluble in absolute alcohol. Exposed to a red heat, it evolves carbonic acid and water, and carbonate of potassa remains. This salt is generally pure, or very nearly so, and may be conveniently resorted to for the preparation of the carbonate and other salts, when purity is required.

CYANIDE OF POTASSIUM (KC_2N or KCy) is obtained by heating to redness, in a covered crucible, a mixture of 8 parts of dry ferrocyanide of potassium, and 3 of dry carbonate of potassa, till it no longer gives off gas: the iron subsides, and the fused product, when poured off, concretes into a white mass, which is a mixture of the cyanide and of cyanate of potassa, the reaction being as follows: $2(K_2FeCy_3)+2(KO,CO_2)=5(KCy)+KO,CyO+Fe_2+2CO_2$. The formation of the *cyanate* may be prevented by adding to the mixture before fusion an eighth of its weight of powdered charcoal; the fused mass may then be digested in boiling alcohol, from which the cyanide of potassium crystallizes on cooling.

Cyanide of potassium should be carefully preserved out of the contact of air and water: it may be fused without decomposition, provided air be excluded, and is not changed by a red heat; but with the access of oxygen it becomes cyanate of potassa: $KCy+2O=KO,CyO$. Its taste is pungent and alkaline, accompanied with the flavor of hydrocyanic acid, and it is very poisonous. It is very soluble in water, and may be obtained from its solution, in anhydrous cubic crystals: it is but little soluble in cold alcohol, which throws it down from its recent and cold aqueous solution: exposed to air, it becomes moist and smells of hydrocyanic acid. It is a powerful reducing agent, as respects oxides and sulphides, and as such is used in mineral analysis; the oxides of copper, and those of tin, iron, and lead, are immediately reduced when sprinkled into the fused cyanide. When cyanide of potassium effervesces with acids, it contains either cyanate or carbonate of potassa: a yellow tint indicates the presence of iron: if it blackens when calcined, it is contaminated by formate of potassa.

CYANATE OF POTASSA (KO,CyO).—The preparation of this salt has been described under CYANIC ACID (p. 262). It is decomposed both by water and acids, which convert the cyanic acid into carbonic acid and ammonia; in fact, by exposure to air, it exhales ammonia, and becomes bicarbonate of potassa. It crystallizes in small plates; tastes like saltpetre; is anhydrous; and in close vessels excluded from air and moisture may be fused without decomposition.

SULPHOCYANIDE OF POTASSIUM (K,C_2NS_2) may be formed by boiling 2 equivalents of finely powdered sulphur in a solution of 1 equivalent of cyanide of potassium: it yields prismatic crystals which are of a cooling bitter taste, deliquescent, and anhydrous. In close vessels this salt fuses, and concretes on cooling into an opaque crystalline mass: heated in the air, it is decomposed, and if moisture be present, carbonate of ammonia and sulphide of potassium are formed. For the chemical characters of this and other sulphocyanides, *see* page 270.

FERROCYANIDE OF POTASSIUM. *Prussiate of Potassa* (K_2,Fe,Cy_3).—When iron filings are digested in a solution of cyanide of potassium, and the mixture is exposed to air, oxygen is absorbed and this compound is produced. If air is excluded, the water is decomposed, and hydrogen is liberated. On evaporation a salt is obtained which has the formula (K_2 FeCy_3,3HO). A mixture of sulphide of iron and cyanide of potassium also forms the ferrocyanide, and sulphide of potassium. When Prussian blue is boiled with potassa it is decomposed, oxide of iron is separated, and on filtering and evaporating the solution, crystals of the ferrocyanide are obtained.

This salt is largely prepared as an article of commerce, chiefly for the use of calico-printers, by calcining at a red heat, in a globular iron vessel, a mixture of carbonate of potassa with animal matters, such as horns and hoofs, woollen rags, or parings of leather. The fused mass takes a portion of iron from the iron vessel, and this forms *prussiate cake.* When cold it is lixiviated, and the evaporated solution yields an impure product, which when redissolved and slowly crystallized, furnishes the purified salt. In this operation the cyanogen derived from the nitrogen and carbon of the organic matter, combines with the potassium and iron to produce the ferrocyanide.

Ferrocyanide of potassium forms permanent yellow, tabular, and octahedral crystals (=K_2,Fe,Cy_3,3HO), of the specific gravity of 1·83: they are insoluble in alcohol. Water at 60° takes up about one-third, and at 212°, its own weight of this salt. It has a bitter, saline, and sweetish taste, and is not poisonous. When moderately heated it loses color, and crumbles into powder, parting with about 13 per cent. of water. By a red heat it is converted with the escape of nitrogen, into carbide of iron and cyanide of potassium: and in the presence of air the latter salt becomes cyanate of potassa, and the iron is oxidized. Boiled with dilute sulphuric or hydrochloric acid, hydrocyanic acid is given out, and a white precipitate is formed similar to that which the salt produces in a solution of protosulphate of iron. By nitric acid or by chlorine it is converted into ferricyanide of potassium. The action of concentrated sulphuric acid upon this salt is attended by the evolution of carbonic oxide. Neither sulphuretted hydrogen, the hydrosulphates, the alkalies, nor tincture of galls, produce any precipitate in solutions of this salt. Red oxide of mercury decomposes it at a moderate heat, peroxide of iron and metallic mercury are precipitated, and cyanide of mercury is formed; so that the iron is peroxidized at the expense of the oxide of mercury. When a solution of this salt forms insoluble precipitates in metallic solutions, the nature of the metal present may often be judged of by the character and color of the precipitate. This is *white* or nearly so, with the salts of manganese, zinc, tin, cadmium, lead, bismuth, antimony, protosalts of iron, mercury and silver; *yellowish-green* with those of cobalt; *reddish-brown*, with those of copper and uranium; *blue*, with the persalts of iron, and *pea-green*, with the salts of nickel. It, therefore, forms a good eliminating or general test for many metals. It is also employed as a reducing agent for arsenic and its sulphides. When a mixture of ferrocyanide of potassium with dilute sulphuric acid is subjected to distillation, hydrocyanic acid is evolved, and a ferrocyanide, represented by the formula K, Fe_2Cy_3, and known as Everitt's *yellow salt*, is among the products (page 265). The following diagram shows the changes which ensue when 6 atoms of sulphuric acid are heated with 2 atoms of crystallized ferrocyanide of potassium.

BEFORE DISTILLATION.				AFTER DISTILLATION.			
	Atoms.	Eqv.			Atoms.		Eqv.
Sulphuric acid	6	240		Bisulphate of potassa	3		384
Cyanide of potassium	4	264		Hydrocyanic acid	3		81
Cyanide of iron	2	108	=	Cyanide of potassium	1	Yellow Salt	66
Water { 6 in the acid 6 in the salt }	12	108		Cyanide of iron	2		108
				Water	9		81
		720					720

Ferricyanide of Potassium (K_3,Fe_2,Cy_6).—When chlorine is passed through a solution of ferrocyanide of potassium till the liquor ceases to precipitate Prussian blue from the persalts of iron, and then filtered and slowly evaporated, it furnishes right rhombic prismatic crystals, which, purified by a second solution, assume a ruby-red color; they are anhydrous, and require 3·8 parts of cold water for solution, and are nearly insoluble in alcohol. They burn with brilliant scintillations, and when heated in close vessels, give off cyanogen and nitrogen, and leave ferrocyanide of potassium and carbide of iron. When dissolved in water, this salt is decomposed by sulphuretted hydrogen, sulphur and cyanide of iron are precipitated, and hydrocyanic acid and ferrocyanide of potassium formed. This salt occasions no precipitate in solutions of iron containing the peroxide only, but it is a most delicate test of the *protoxide*, with which it forms a blue precipitate. In its formation the chlorine abstracts one-fourth of the potassium of the ferrocyanide, producing chloride of potassium and ferricyanide, $2(K_2,Fe,Cy_3)+Cl,=KCl+K_3,Fe_2,Cy_6)$.

Silicates of Potassa.—When silica and potassa are fused together they combine in various proportions and produce a series of silicates, differing in solubility and fusibility, according to the preponderance of the base or of the acid. When the alkali is in excess, the product is soluble in water; but with excess of silica it is insoluble, and constitutes a species of glass (*see* Silicate of Soda). When finely divided silica is added to fused carbonate of potassa, carbonic acid is evolved, and by using atomic proportions, a compound may be obtained represented, by KO,SiO_3, in which 47 parts of potassa are united to 46 of silica. When 1 part of silica and 4 of caustic potassa are fused together and slowly cooled, a part of the compound may be poured out of the crucible before the whole has solidified, and pearly crystals are formed in the residuary portion.

Tests for Potassa and its Salts.—A solution of *pure potassa* is characterized—1. by a strong alkaline reaction on test-paper; 2. by its giving a brown precipitate with a solution of nitrate of silver (oxide of silver). This distinguishes it from solutions of carbonate and bicarbonate of potassa, both of which give a yellowish-white precipitate (carbonate of silver); 3. The solution gives a crystalline precipitate of acid tartrate of potassa, when a large excess of a concentrated solution of tartaric acid is added to it. The solution must not be too dilute. The precipitate is soluble in 180 parts of water, and is readily dissolved by mineral acids and by alkaline solutions. The addition of a small quantity of alcohol promotes this reaction; 4. Chloride of platinum gives with the solution a yellowish precipitate of platinochloride of potassium ($KCl,PtCl_2$) (100 parts of this precipitate, when dried, correspond to 16·03 of potassium, 19·33 of potassa, and 40·39 of platinum); 5. A clean platinum wire dipped into the solution, and introduced into a smokeless flame, gives a pale violet color to it. A small quantity of the liquid, burnt with alcohol in a platinum capsule, will give a similar color to the flame.

The solution of potassa is precipitated by the solutions of the picric, perchloric, and fluosilicic acids. The last is frequently employed for separating the acid from its salts (page 288).

The solutions of the salts of potassa when sufficiently concentrated, give precipitates with tartaric acid and chloride of platinum, similar to those obtained with the solution of the pure alkali. In the smallest quantity on platinum wire, they tinge flame of a pale violet color. This color is perceptible through blue glass, or a diluted solution of sulphate of indigo. In using chloride of platinum to detect potassa-salts, the absence of ammoniacal salts must be previously ascertained, as they produce analogous effects upon this reagent; or the platinum-test may be applied after the salt has been subjected to a red heat, by which the salts of ammonia will have been decomposed or evaporated. When chloride of platinum is used in quantitative analysis, it should be added in excess to the potassa-solution, together with a drop or two of hydrochloric acid, and the mixture evaporated at 212°. The residue should then be washed with a mixture of equal parts of proof spirit and water, which removes everything except the platino-chloride of potassium.

CHAPTER XXIV.

SODIUM (Na=23).

SODIUM (*Natrium*) was discovered by Davy in 1808. It is obtained from carbonate of soda by a process similar to that for potassium. It is soft, malleable, and easily sectile: it does not, like potassium, become brittle at 32°, but even at that low temperature several globules may be welded together by pressure. In color it somewhat resembles silver, but rapidly tarnishes on exposure to air. Its sp. gr. is 0·97. It softens at about 122°; it fuses at about 200°, and is volatile at a white heat, its vapor being colorless. It burns with a yellow flame when heated in contact with air, and requires the same cautions to preserve it from oxidizement as potassium. Sodium, when placed on a large surface of cold water, does not take fire and burn like potassium. It decomposes the water without combustion. If, however, one or two drops of water are placed on a fresh-cut slice of sodium, the heat is so intense, that it immediately takes fire and burns with a yellow flame. If wrapped in a small muslin bag, and placed on water, or even on ice, the metal will also take fire and burn.

SODIUM AND OXYGEN; PROTOXIDE OF SODIUM; SODA; (NaO).—The affinity of sodium for oxygen appears to be somewhat less than that of potassium. It is more slowly oxidized on exposure to air; but the protoxide is the result of the action of air or water. *Anhydrous soda* is obtained in the same way as anhydrous potassa, and resembles it in appearance, but is less fusible and less volatile.

PEROXIDE OF SODIUM (Na_2O_3).—By heating sodium in oxygen, it burns vividly, and a yellowish-green *peroxide* is formed, which, by the action of water, evolves oxygen, and produces a solution of the protoxide.

HYDRATE OF SODA; CAUSTIC SODA (NaO,HO) is obtained from the *carbonate*, by the action of lime, as described under the head of *Potassa*. Hydrate of soda is white, opaque, brittle, and deliquescent; its sp. gr. is 2·0;

it requires a red heat for fusion ; and when intensely heated evaporates and tinges the flame yellow. It has the same general characters as hydrated potassa ; like it, it retains water at a red heat, and is deprived of it by the same means.

The following table shows the proportion of anhydrous soda in solutions of different specific gravities :—

Specific gravity of solution.	Dry soda per cent. by weight.	Specific gravity of solution.	Dry soda per cent. by weight.
1·85	63·6	1·36	26·0
1·72	53·8	1·32	23·0
1·63	46·6	1·29	19·0
1·56	41·2	1·23	16·0
1·50	36·8	1·18	13·0
1·47	34·0	1·12	9·0
1·44	31·0	1·06	4·7
1·49	29·0		

Hydrated soda is distinguished from hydrated potassa by forming an *efflorescent* paste when long exposed to the atmosphere : potassa under the same circumstances, remains deliquescent. The chemical properties of the solution of soda as an alkali, are similar to those of potassa. It may also contain the same impurities: oxide of lead is frequently present in it, as the result of a chemical action on the glass. This impurity is detected by the addition of sulphuretted hydrogen or sulphide of ammonium, either of which will give a brown color to the liquid, if lead should be present.

CHLORIDE OF SODIUM ; SEA SALT ; MURIATE OF SODA ; (NaCl).—Sodium when heated in chlorine burns vividly, and produces this compound. It exists abundantly in nature both as a solid fossil, (*sal gemme*), and in the ocean, and in brine-springs. Extensive beds of it occur in Cheshire, where it is known under the name of *rock-salt.* From these sources the immense demands are supplied ; that is, either by evaporating brine-springs, or sea-water, or quarrying it from the mine. In sea-water it amounts to about 2·7 per cent., or to about 4 ounces in the gallon. When heated, chloride of sodium *decrepitates.* At a red heat it fuses without undergoing decomposition, and on cooling concretes into a white mass ; at a bright-red heat it sublimes, and tinges flame of a blue color. It is insoluble in absolute alcohol, but dissolves in proof spirit. It is taken up nearly in the same proportion by cold and by hot water ; 100 of water dissolving 37 of salt ; or 1 of salt to 2·7 of water. Concentrated hydrochloric acid precipitates chloride of sodium from its concentrated aqueous solution. When pure, chloride of sodium does not alter by exposure to air, though it is generally more or less deliquescent, from containing chlorides of magnesium and calcium. Obtained by slow or spontaneous evaporation, it crystallizes in solid cubes ; but when procured at a boiling heat, by removing its crystals from the surface of its solution, it forms hollow quadrilateral pyramids. The crystals are anhydrous, though they often include interstitial water. Their specific gravity is 2·557.

Chloride of sodium is decomposed by moist carbonate of ammonia ; bicarbonate of soda, sal-ammoniac and free ammonia are formed ; with moist carbonate of potassa, it yields chloride of potassium and carbonate of soda. In the process for obtaining hydrochloric acid it is decomposed by sulphuric acid. In this decomposition, the oxygen of the water of the sulphuric acid is transferred to the sodium of the salt, the chlorine of which combines with the hydrogen of the water to produce hydrochloric acid, and the oxide of sodium unites with the dry sulphuric acid to produce sulphate of soda ($NaCl+SO_3,HO=NaO,SO_3+HCl$). Chloride of sodium is also decomposed by nitric acid : effervescence ensues, chlorine tinged with nitrous acid is evolved, and, provided a sufficiency of nitric acid has been used, nitrate of soda remains on evaporation to dryness. When chloride of sodium is triturated with oxalic acid and heated hydrochloric acid is evolved, and oxalate of soda formed, so that when the residue is heated to redness, carbonate of soda remains. When chloride of sodium and ferruginous clay are heated together, the silica and alumina of the clay are vitrified by the soda of the salt, and its chlorine combines with the iron; it is upon this principle that salt is used as a glaze for stoneware; when thrown into the furnaces in which the articles are baked, it is volatilized, and decomposed upon their surfaces. It is of most extensive use as a preservative of food; as a condiment; as a source of soda, of hydrochloric acid, and chlorine; and for various agricultural and horticultural purposes.

CHLORIDE OF SODA; CHLORITE OF SODA; HYPOCHLORITE OF SODA.—These names have been applied to a compound formed by passing chlorine into a cold and dilute solution of caustic soda, or by decomposing chloride of lime by a solution of carbonate of soda. It is powerfully bleaching, and smells of chlorine: exposed to air, it absorbs carbonic acid and evolves chlorine. When heated it undergoes changes similar to those produced by passing chlorine into a solution of soda, that is, chlorate of soda and chloride of sodium are formed.

Labarraque's disinfecting liquid, which is essentially a hypochlorite, is made by passing chlorine into a solution of carbonate of soda (*see* page 314).

BROMIDE OF SODIUM ($NaBr$).—Sodium and bromine act upon each other with much intensity; the result is a fusible compound, soluble in water and in alcohol, and crystallizing at 86° in anhydrous cubes, but at lower temperatures in hexagonal tables, containing 26·37 per cent. of water.

IODIDE OF SODIUM (NaI).—Iodine and sodium act upon each other with the same phenomena as in the case of potassium. Iodide of sodium may also be formed by adding iodine to a solution of caustic soda, evaporating to dryness, and fusing the residue. It is contained in the mother-liquor of kelp, in the ashes of burned sponge, and in the oyster. (*See* IODINE, p. 189.)

NITRATE OF SODA (NaO,NO_5).—This salt (formerly called *cubic nitre*) may be obtained by neutralizing carbonate of soda by dilute nitric acid. It crystallizes in rhomboids, soluble in 3 parts of water at 60°. It has a cool sharp flavor, and is somewhat deliquescent in damp air, and therefore unfit for the manufacture of gunpowder. A mixture of 5 parts of nitrate of soda, 1 of charcoal, and 1 of sulphur, burns more slowly than a similar mixture with nitrate of potassa: its flame is yellow. Large quantities of *native nitrate of soda* occur in Peru, forming a stratum covered with clay and alluvium, of many miles in extent, and it is now a considerable article of trade. It may be employed in fireworks, and used as a substitute for nitre (it being cheaper) in the manufacture of nitric acid, of sulphuric acid, and in other cases in which nitre is consumed. It is too expensive as a source of soda. It is frequently employed as a manure. At a red heat it is decomposed with results similar to those of nitrate of potassa, and is ultimately resolved into soda, nitrogen, and oxygen. It has been suggested as an economical source of oxygen for the supply of the *lime light*.

SODIUM AND SULPHUR.—The account of the action of sulphur on potassium and potassa, and of sulphuretted hydrogen upon solution of potassa, applies generally to sodium and soda, and their corresponding compounds.

HYPOSULPHITE OF SODA (NaO,S_2O_2).—This salt may be procured by the various processes which have been described at page 283. It is now manufactured on a large scale for the purpose of photography, and is usually seen in prismatic crystals. It is very soluble in water. Its solution has a bitter, nauseous taste. It is decomposed by heat. Its chemical properties have been elsewhere fully described (p. 208).

SULPHITE OF SODA (NaO,SO_2) is obtained in the same way as sulphite of potassa: it is crystallizable in prisms, soluble in four parts of water at 60°. The crystals contain 8 atoms of water. There is also a crystallizable *bisulphite of soda*, obtained by passing a current of sulphurous acid gas through a solution of carbonate of soda till fully saturated; it yields on evaporation, four-sided rectangular prisms, having a sulphurous taste and smell, and reddening vegetable blues.

SULPHATE OF SODA; GLAUBER'S SALT; SAL MIRABILE (NaO,SO_3); is abundantly produced in various processes of the arts, by the action of oil of vitriol upon chloride of sodium: $SO_3,HO,+NaCl=NaO,SO_3+HCl$. Anhydrous sulphate of soda may be obtained by drying the common hydrated crystals upon a sand-heat; they fall into a white powder, which reabsorbs water with the evolution of heat. When a hot concentrated solution of sulphate of soda is suffered to deposit crystals (at a temperature between 90° and 100°) they are anhydrous rhombic octahedra. 100 of water at 57° dissolve 10·58 of this anhydrous salt, and the solution, set aside to cool and crystallize, gives the common decahydrated crystals. The ordinary crystals (decahydrated sulphate of soda) are deposited from solutions cooled to common temperatures; they are large transparent striated prisms. They are efflorescent, and by due exposure to dry air, lose their water, crumbling into powder, which, however, in damp air, reabsorbs water, with increase of bulk. When gently heated, the crystals fuse, and at the same time deposit anhydrous sulphate; their taste is saline and slightly bitter; they are insoluble in alcohol. The solubility of sulphate of soda in water follows a singular law. After having increased rapidly to about the temperature of 92°, where it is at its maximum, it diminishes to 215°, and at that temperature the salt is nearly of the same solubility as at 87°.

BISULPHATE OF SODA ($NaO,2SO_3$) is obtained by adding sulphuric acid to a hot solution of sulphate of soda. It crystallizes in rhombic prisms, soluble in twice their weight of water at 60°, and containing water of crystallization. By adding half an equivalent of oil of vitriol to sulphate of soda, and evaporating the solution, crystals of a *sesquisulphate*, $2NaO,3SO_3$, are deposited.

PHOSPHATES OF SODA.—1. *Tribasic phosphates.*—There are three phosphates of soda belonging to the tribasic class: they have been usually distinguished as *common* or *rhombic phosphate*, *subphosphate*, and *biphosphate*. The *ammoniophosphate* also belongs to this class.

Common or *rhombic phosphate*, $2(NaO),HO,PO_5+24HO$. This salt (the *sal perlatum* of old writers), is obtained by saturating the phosphoric acid prepared from calcined bones by sulphuric acid, with carbonate of soda: the liquor is filtered, evaporated, and set aside to crystallize. The crystals are alkaline to test-paper, superficially efflorescent, and soluble in about 4 parts of cold water. This salt has a slightly saline and alkaline flavor, and has been used in medicine as an aperient. The crystals when moderately heated, fuse in their water of crystallization; at a dull red-heat, the salt runs into a clear glass, which becomes opaque on cooling (*pyrophosphate*). When a solution of this phosphate is dropped into nitrate of silver, it forms a yellow precipitate (p. 226).

Subphosphate of Soda, $3[NaO]PO_5+24HO$.—When excess of caustic soda is added to a solution of the preceding salt, it yields on evaporation slender six-sided prisms, which are permanent in the air, soluble in 5 parts of water at 60°, and undergo watery fusion at 170°. The solution of this salt absorbs carbonic acid, and is deprived of one-third of its alkali by the weakest acid. This salt continues tribasic after exposure to a red heat.

Biphosphate of Soda, $NaO,2(HO),PO_5+2HO$, is obtained by adding terhydrated phosphoric acid (p. 273) to a solution of the common phosphate, till it ceases to precipitate chloride of barium. The solution in cold weather affords crystals, which are very soluble, and have a distinctly acid reaction. It precipitates nitrate of silver of a yellow color.

Ammoniophosphate of Soda (NaO,NH_4O,HO,PO_5+8HO).—This salt exists in urine, whence it was procured by the early chemists under the names of *microcosmic* and *fusible salt.* It may be formed by dissolving in water 5 parts of crystallized rhombic phosphate of soda with 2 of crystallized phosphate of ammonia, and evaporating. It forms transparent prisms of a saline and cooling taste, very soluble, and which effloresce and lose ammonia in a dry atmosphere.

2. *Bibasic Phosphates. Pyrophosphates.*—There are two phosphates of soda belonging to this class, commonly called the *pyrophosphate* and *bipyrophosphate.*—*Pyrophosphate of Soda* [$2(NaO,)\ PO_5+10HO$] is obtained by heating the common phosphate to redness, when it loses its basic water and water of crystallization, and becomes *anhydrous pyrophosphate,* $=2[NaO,]\ PO_5$. Dissolved in hot water, this anhydrous salt yields permanent prismatic crystals on cooling, containing 10 atoms of water; these crystals are less soluble than those of the common phosphate, and their solution precipitates nitrate of silver, *white,* and has an alkaline reaction. The insoluble pyrophosphates, with the exception of that of silver, are soluble to a certain extent in the solution of pyrophosphate of soda. The pyrophosphates of ammonia and of potassa exist in solution, but when they crystallize they pass into tribasic salts (p. 228).

Bipyrophosphate of Soda (NaO,HO,PO_5).—This salt is formed by the application of a graduated heat to the biphosphate of soda; its solution has an acid reaction, and does not crystallize. It throws down white pyrophosphate of silver from nitrate of silver.

3. *Monobasic Phosphates; Metaphosphate of Soda* (NaO,PO_5).—When any of the preceding phosphates which contain only 1 equivalent of fixed base (soda) are heated to redness, they afford *metaphosphate:* when bipyrophosphate is used, the properties of the resulting salt vary with the temperature to which it has been subjected; thus if heated to 500°, it becomes *neutral,* but still retains the characters of a pyrophosphate. At a temperature somewhat higher, but below redness, it becomes very difficultly soluble, and only feebly acid; when evaporated, its solution does not give crystals, but dries into a transparent pellicle like gum, which retains at the temperature of the air somewhat more than a single equivalent of water. Added to neutral and not very dilute solutions of earthy and metallic salts, metaphosphate of soda throws down insoluble hydrated metaphosphates, of which the physical condition is remarkable; they are all soft solid or semifluid bodies, the metaphosphate of lime having the degree of fluidity of Venice turpentine (p 226).

CARBONATE OF SODA (NaO,CO_2).—This important salt was formerly obtained by the combustion of marine plants, the ashes of which afforded by lixiviation the impure alkali called *soda.* Two kinds of rough soda were known in the market, *barilla* and *kelp;* besides which, some *native carbonate of soda* was also imported from Egypt. *Barilla* is the semifused ash of the *salsola soda. Kelp* is the ash of sea-weeds, collected upon many of the rocky coasts of Britain. It seldom contains more than 5 per cent. of carbonated alkali, and about 24 tons of sea-weed are required to produce 1 ton of kelp. The best produce is from the hardest deep-sea *fuci*, such as the *serratus*, *digitatus*, *nodosus*, and *vesiculosus*.

Kelp is now chiefly important as a source of iodine, the large commercial demands for carbonate of soda being supplied by the decomposition of sulphate of soda. The process consists, 1. In the conversion of chloride of sodium into sulphate of soda or *salt cake*. 2. In the production of *black ash*, by heating sulphate of soda with chalk and coal. 3. In the extraction of *carbonate of soda* from the black ash. The furnace in which the chloride of sodium is decomposed consists of an iron vessel of the shape of a flattened sphere, having two openings, one in front, for the introduction of the charge, and the other opposite to it, through which the charge is thrust out into the *roaster*. From the upper part of the decomposing pan a pipe issues for the conveyance of the hydrochloric vapors into the *condenser*, which consists of two or more lofty turrets communicating with each other and filled with large pebbles, or with fragments of coke, and through each of which a stream of water is allowed slowly to flow (from a reservoir at the summit), which having absorbed the hydrochloric gas, runs off at the bottom into a receiver. The gases or vapors enter the first tower at its base, and passing upwards, are conveyed, by a pipe of communication, into the upper part of the second tower, through which they pass downwards. The hydrochloric acid is thus removed, and the uncondensable gases pass off into a lofty chimney with which the base of the second tower is connected by a flue; in this way a current of air is constantly drawn from the decomposing pans, and from the part of the furnace called the *roaster*, which is also supplied with a separate pipe communicating with the condensing towers. In the decomposing pans, the original charge of sulphuric acid and salt, is converted into a mixture of bisulphate of soda and undecomposed chloride; but when the charge is pushed on into the second division of the furnace, or roaster, the decomposition is completed by the higher heat, and the bisulphate of soda, acting on the undecomposed chloride, converts the whole into neutral sulphate, or *salt cake*. In the next step of the process, this rough sulphate of soda is mixed with its weight of bruised chalk or limestone, and somewhat less than its weight of small coal. This mixture is heated and ultimately fused in a proper furnace, during which it gives out jets of inflammable gas; and when these cease, the charge is raked out into iron barrows, and in this state it is called *ball soda* or *black ash*. This is then broken up and lixiviated with warm water, so as to extract all that is soluble; the solution is allowed to settle, and then evaporated in shallow pans, and the product so obtained is mixed with sawdust and roasted in a reverberatory furnace; it thus yields the crude carbonate of soda known under the name of *soda ash*, and from this the purified *crystallized carbonate* is obtained. The chemical changes concerned in the above operations are chiefly these: when, as in the preparation of black ash, sulphate of soda is fused with carbon and carbonate of lime, carbonic oxide is evolved and sulphide of sodium formed; this and the carbonate of lime then react on each other so as to form carbonate of soda and sulphide of calcium, the latter being combined with excess of lime so as to be insoluble in water. 1 equivalent of sulphate of soda, 1 of carbonate of lime, and 4 of carbon, would thus produce 1 of carbonate of soda, 1 of sulphide of calcium, and 4 of carbonic oxide, $NaO,SO_3+CaO,CO_2+4C=NaO,CO_2+CaS+4CO$. Some other processes for the production of carbonate of soda from common salt have been proposed, but none have hitherto superseded the above.

The usual form of the common crystallized carbonate of soda is a rhombic octahedron. It is soluble in twice its weight of water at 60°, and in less than its own weight at 212°. Its taste and reaction are alkaline. It fuses readily in its water of crystallization, and on pouring off the fused salt, a portion of monohydrated carbonate remains. Exposed to a dry atmosphere, the crystals effloresce, and at a red heat lose the whole of their water. When the vapor of a boiling solution of carbonate of soda is introduced into a flame, it gives it a yellow color, in consequence of traces of the salt passing off with the aqueous vapor. Crystals containing smaller proportions of water may be obtained, but these rarely occur, and the usual crystals are, $NaO,CO_2,10HO$. The principal impurities contained in carbonate of soda are detected as follows: 1. *Sulphate of soda.* A precipitate by chloride of barium when the solution is supersaturated with hydrochloric acid. 2. *Chloride of sodium.* By a precipitate with nitrate of silver in the solution supersaturated by nitric acid. 3. *Salts of potassa,* by chloride of platinum, or tartaric acid. 4. *Lime,* by oxalic acid. Carbonate of lime is rendered soluble to a certain extent by carbonate of soda, and such a solution cooled to 32° deposits a white crystalline powder composed of the two carbonates. *Oxide of lead* from flint glass is detected by the solution giving a brown precipitate with sulphide of ammonium.

CHLORINATED CARBONATE OF SODA.—By proper management, chlorine may be combined with a solution of carbonate of soda; the resulting combination has been termed *Labarraque's disinfecting liquid.* It is obtained as follows: 2800 grains of crystallized carbonate of soda are dissolved in 1·28 pints of water, and the chlorine slowly evolved from a mixture of 967 grains of salt with 750 grains of black oxide of manganese, and 967 grains of sulphuric acid, previously diluted with 750 grains of water, is carefully passed into it. No carbonic acid escapes, and a pale yellow liquid is the result; its taste is sharp, saline, and astringent, and it at first reddens, and then bleaches turmeric paper. It is but little changed by a boiling heat, and gives out no chlorine. By *careful* evaporation, it furnishes crystals which produce the original liquid when redissolved; but exposed to the air, and suffered to evaporate spontaneously, the chlorine escapes, and crystals of carbonate of soda are obtained.

BICARBONATE OF SODA ($NaO,HO,2CO_2$) is formed by passing carbonic acid through a strong solution of the carbonate; a granular or crystalline powder is deposited, which, when carefully dried at common temperatures, is composed as above. This salt may also be obtained by condensing carbonic acid upon crystals of the carbonate; a portion of the water of the latter salt separates, and when the gas ceases to be absorbed, it is found converted into a porous and friable bicarbonate, which must be carefully dried at a low temperature, otherwise it loses a portion of its carbonic acid. Bicarbonate of soda has a slight alkaline taste and reaction. It is much less soluble than the carbonate, requiring 10 of water at 60°. The crystals of this bicarbonate are rectangular prisms. It loses carbonic acid if moistened and left in the vacuum of an air-pump: the gas is also evolved when 1 part of the salt is boiled with 4 of water. In these cases it is converted into a *sesquicarbonate.* When long exposed to damp air, it is converted, after some months, into pentahydrated monocarbonate ($NaO,CO_2,5HO$). Its solution gives no precipitate with sulphate of magnesia, while a solution of the carbonate is immediately precipitated.

SESQUICARBONATE OF SODA ($2NaO,3CO_2$).—This carbonate of soda occurs *native* in the Soda Lakes of Hungary; also in Africa, near Fezzan, where the natives call it *Trona:* it is in hard striated crystalline masses, not altered by exposure to air: a productive soda lake also exists in South America, at Maracaibo.

CARBONATE OF SODA AND POTASSA (NaO,CO_2+KO,CO_2) is obtained by fusing the salts in single atomic equivalents: the double salt is much more fusible than its components, and is therefore conveniently used in many cases of mineral analysis by fusion, as in the analysis of insoluble silicates (page 286). When dissolved in water the component carbonates separate.

BORATE OF SODA; BORAX; BIBORATE OF SODA; ($NaO,2BO_3$).—This salt, formerly imported from India, under the name of *Tincal*, is now manufactured by combining soda with the native boracic acid procured from Tuscany. Common borax crystallizes in transparent prisms, slightly efflorescent. Its taste is cooling and alkaline; it has an alkaline reaction upon turmeric. It is soluble in 12 parts of cold, and 2 of boiling water. When heated it loses water of crystallization, and becomes a porous friable mass, called *calcined borax*. At a red heat it runs into a transparent glass, which, by exposure to air, becomes opaque and pulverulent upon the surface. The common crystallized borax is a decahydrate$=NaO,2BO_3,10HO$. This salt is decomposed by the greater number of the acids. (*See* BORACIC ACID, page 276.) It is often used as a blowpipe flux for vitrifying metallic oxides, and forming beads of different colors: violet with manganese; green with iron, chromium and copper; blue with cobalt; and slightly yellow with some of the colorless oxides. In the reduction of the metals by charcoal, borax is often useful as forming a medium through which the globules fall and collect into a button, being at the same time protected from the air. At the potteries it is used in the glazes applied to the better kinds of earthenware, and to porcelain. Alone, or mixed with phosphate of ammonia or soda, borax may be employed to render muslin, paper, wood, and other materials, to a certain extent incombustible; this it does by covering them with a vitrifiable glaze by which the access of air is prevented. Borax is also used in the process of *soldering;* when, for instance, two surfaces of copper are to be soldered together, they are scraped or rubbed clean, sprinkled with a mixture of powdered borax and solder-filings, and heated till the solder fuses so as to alloy with the copper and make a perfect joint: the borax not only prevents the contact of air, and consequent oxidation of the metals, but dissolves any oxide accidentally formed, and so retains the surfaces in that perfectly clean state which is requisite for their union. An aqueous solution of borax dissolves several of the resins, and some of these solutions, especially that of lac, form good vehicles for coloring materials.

OCTAHEDRAL BORAX ($NaO,2BO_3,5HO$).—This salt contains 5 instead of 10 atoms of water, and is obtained by dissolving common borax in boiling water, till the solution has a specific gravity of 1·26; it is then allowed to cool slowly, and between the temperatures of 174° and 145° it deposits octahedral crystals; below that temperature, the ordinary prismatic crystals are formed. Octahedral borax is harder than the prismatic, and is preferred for brazing and soldering.

SILICATES OF SODA.—The atomic constitution of these silicates is as indefinite as those of potassa. By the fusion of one equivalent of anhydrous carbonate of soda with 1 of silica, $53+46$, a silicate is formed, which when dissolved in a small quantity of water yields crystals of a silicate containing 6 and 9 atoms of water. When 100 parts of silica are fused with 40 of caustic soda, the resulting glass is transparent; but if slowly cooled exhibits crystalline points. When 8 parts of dry carbonate of soda, 15 of fine white sand or powdered flint, and 1 part of powdered charcoal are well mixed and fused, a glass is obtained which is soluble in about 6 parts of boiling water: this solution has been used to diminish the combustibility of wood, canvas, and similar materials, and more especially of theatrical scenery: it prevents its burning with flame, by forming a glaze upon the surface. Silicates of soda always have a greenish or bluish tint, however pure the materials used in their production, and this is an obstacle to the substitution of soda for potassa in certain kinds of glass.

Manufacture of Glass.—Glass is a compound of silica with potassa or soda, other substances, or silicates, more especially those of lead, lime, or iron, being occasionally added; transparency and insolubility in water being among its most essential qualities. It should also resist the action of other solvents, such as acids and alkalies, and for many purposes, it should not fuse or even soften at a red heat. The insolubility of glass depends much upon its aggregation, for if reduced to fine powder it reddens turmeric paper when moistened, and restores the blue color to red litmus, and a portion of the alkali is frequently abstracted from glass long exposed to the action of air and water; so also the glasses containing oxide of lead are readily discolored by sulphuretted hydrogen, when in powder and diffused in water, although they long resist its action when in their ordinary state. The more fusible glasses, containing excess of alkali, of oxide of lead, or of lime, are also apt to be acted on by acids and alkalies, and are unfit for the retention of such solutions; and all glass is more or less disintegrated by the action of water at very high temperatures.

As the varieties of glass are mixtures rather than definite compounds of their component silicates, they scarcely admit of being represented by formulæ, though in some cases the proportion which the oxygen of the bases bears to that contained in the silica may be usefully stated. The large proportion of oxide of lead in *flint-glass* gives it a high refractive power and brilliancy when cut, but renders it soft, easily fusible, and liable to be acted on by many chemical agents. In *plate-glass* the predominance of silicate of soda gives a more liquid combination than potassa, and enables it to be poured out of the crucible in which it is melted, upon a cast-iron table, and rolled into sheets, which, after careful annealing, are ground to a level surface with emery, and ultimately polished with colcothar. Large quantities of the waste and broken glass of former operations, are frequently melted up (under the name of *cullet*) with the materials in the crucible. The remarkable tenacious viscidity of glass, when in a fit state for the operations of the glass-house, and the facility with which it is shaped, by blowing, moulding, and other manipulations, into its infinitely various forms, can only be understood by personal inspection.

The following table will give a notion of the relative proportions of the components of several kinds of glass in common use, but these vary to such an extent as not to admit of being represented by any satisfactory formulæ. A glass composed of borate and silicate of lead has been used by Faraday for some optical purposes, and the borosilicate of zinc has been similarly applied by Maez and Clemandot.

	Plate.	Crown.	Flint.	Bottle.	Tube.	Optical.
Silica	78	63	52	59	73	43
Potassa	2	22	14	2	12	12
Soda	13	...	...	10	3	
Lime	5	12	...	20	11	1
Alumina	2	3	1	2	1	
Oxide of lead . .	...	...	33	...	...	44
Oide of iron . .	...	...	...	7	...	
	100	100	100	100	100	100

All glass requires to be carefully *annealed*—that is, suffered to cool very slowly—otherwise it becomes liable to fly to pieces upon the slightest touch of any substance hard enough to scratch its surface. Small unannealed flasks, blown from samples taken from the pot, for the purpose of ascertaining the quality of the glass, and known in the glass-house under the name of *proofs*, will show this. When a fragment of flint is dropped into them they immediately crack; and if melted bottle-glass be dropped into water, so as to form what are called *Rupert's drops*, the instant that their thin end is broken off they crumble into powder with a kind of explosion. This probably arises from the unequal tension of the layers of glass in consequence of the sudden cooling of the exterior, whilst the interior remains dilated, or even red-hot. When large masses of glass are slowly cooled, crystallized nodules are sometimes formed, more or less opaque, and imbedded in the transparent glass. These appear to arise from the formation of definite silicates.

When glass, imbedded in sand, is heated up to a point a little below that of fusion, and allowed to cool slowly, it is converted into *Reaumer's porcelain:* it has become hard, white, opaque, and somewhat less fusible; changes which have been referred to the formation of certain definite crystallizable silicates, more especially those of lime and alumina. These phenomena of *devitrification* are best shown with common green bottle-glass.

A peculiar glass is used for the manufacture of artificial gems, called *strass* or *paste*, containing a large quantity of oxide of lead, and frequently borate of lead: it is easily fusible, highly refractive, and very soft.

The art of *coloring glass* depends upon its power of dissolving certain metallic oxides. The principal metals thus employed are, 1. *Gold;* it imparts various shades of red or pink, inclining to purple. 2. *Silver;* oxide, chloride, or phosphate of silver, give a yellow color. 3. *Iron.* The oxides of iron produce blue, green, yellow, or brown, dependent upon the state of oxidation and quantity. The protoxide gives various shades of green; the peroxide of brownish yellow. 4. *Manganese.* The protoxide leaves the glass colorless, but the peroxide gives it various tints of violet, and, if added in excess, renders it black. This oxide was formerly called *glass soap*, from its property of destroying the green tint communicated by protoxide of iron, derived from the use of impure materials; this it effects by converting the protoxide of iron into peroxide, which, in small proportions, does not materially affect the color of the glass; whilst the peroxide of manganese, losing oxygen, becomes protoxide, and in this state is also not injurious. A little nitre is sometimes used for the same purpose. 5. *Copper.* The protoxide gives a rich green, and the dioxide a ruby red. The glittering appearance of *aventurin* glass is due to the dissemination of minute crystals of metallic copper, produced by the fusion of a mixture of iron and copper scales in the glass. 6. *Cobalt,* in the state of oxide, gives beautiful blues of all shades; in large quantity black. 7. *Chromium* produces greens and red, depending upon its state of oxidation. 8. *Uranium* is the source of the peculiar opalescent yellowish-green glass. 9. *Tin,* in the state of binoxide gives the varieties of opalescent glass, terminating in opaque white *enamel*, in which there is also a little oxide of lead. An alloy of 1 part of tin and 2 of lead is calcined for the production of the oxides, and these are mixed with powdered glass. When surfaces are to be enamelled, this mixture is applied with a brush, and then fused by exposure to heat in a muffle. The colors used in enamel painting are derived from the metals above enumerated. A species of enamel is sometimes applied to iron saucepans and other vessels; it is a vitrifiable mixture of powdered flint with carbonate of soda, borax, and Cornish clay, with a little oxide of tin; this is brushed over the surface, then carefully dried, and heated in a muffle to bright redness; 10. *Arsenic.* Arsenious acid is much employed for giving an *opal* tint to glass. This glass is translucent, of a pale bluish-white color, with a reddish hue when viewed in certain lights. On powdering this glass, and applying the usual tests for arsenic, the presence of this substance may be readily detected. Arsenious acid, in small quantity, by peroxidizing iron, which usually gives a green tint, tends to render glass colorless. The metal arsenic is volatilized in this process; hence arsenic is not found in glass-tubing, or in ordinary chemical glass.

SODIUM AND POTASSIUM form an *alloy* which, if composed of 1 part of potassium, and 3 of sodium, remains fluid at 32°. Equal parts of the metals form a brittle crystallizable alloy. When added to a small quantity of mercury they form a solid amalgam, with the production of great heat and a partial combustion of the alkaline metals.

TESTS FOR SODA AND ITS SALTS.—Pure soda and its carbonates, like pure potash and its carbonates, have, in solution, an alkaline reaction, and produce with a solution of nitrate of silver similar precipitates. The differences between these alkalies are chiefly of a negative kind. Thus a solution of soda gives no precipitate with a concentrated solution of tartaric acid, or of chloride of platinum. It is not precipitated by picric or perchloric acid. When neutralized by nitric acid and crystallized, soda yields rhombic plates, while, under the same circumstances, potassa yields long prisms. The essential character of soda is that in the smallest quantity it will give a well-marked yellow color to the flame of alcohol, either when burnt with a small portion of that liquid, or when a minute film of the alkali, on a fine platinum wire, is introduced into the flame of a spirit-lamp. This color is very powerful, and tends to conceal the pale violet tint given by potassa. Unless the soda flame is very intense, it will, however, be intercepted by blue glass, or a diluted solution of indigo; so that if potassa is mixed with soda, the pale violet color of the potassa flame only will be seen through this colored medium. The delicacy of these colored reactions of the alkalies has been elsewhere adverted to (p. 58). Imponderable traces of sodium may be detected by the aid of a fine platinum wire, and by spectral analysis it is found that potassium and sodium give perfectly distinct spectra, which serve to identify them and to determine the fact of their admixture, when no other chemical means are available for this purpose. The *salts of soda* are very soluble in water; they give the same negative results with tests as the pure alkali. They are readily distinguished by the strong yellow light imparted to flame.

CHAPTER XXV.

LITHIUM. CÆSIUM. RUBIDIUM.

LITHIUM (Li=7).

LITHIA, which is the oxide of this metal, was discovered by Arfwedson, in 1817. To obtain lithium, its chloride may be decomposed by an electric current. The metal is reddish-white, softer than lead, and admits of welding and of being pressed into wire: it is the lightest known solid, its specific gravity being 0·594, so that it floats on naphtha; it fuses at 356°, but is not volatile at a red heat. It decomposes water without combustion, setting free hydrogen. It forms only one oxide. When heated in air it burns with an intensely white light, forming lithia.

LITHIA (LiO) has only been found in a few minerals; and, by spectral analysis, in minute quantities in the sea and many mineral waters. By this delicate method of research, traces of it have been detected in the Thames water, fireclay, and a variety of other substances—*Lepidolite, triphane,* and *petalite*; are the principal minerals from which it has been obtained, in proportions varying from 3 to 6 per cent. The mineral, in very fine powder, is intensely heated in a covered platinum crucible, with about twice its weight of lime for half an hour. The resulting mass is then digested in diluted hydrochloric acid, and the whole evaporated to dryness; when this residue is dissolved in dilute sulphuric acid, and the solution is treated with oxalate of ammonia to separate lime, and with baryta water to separate sulphuric acid, it yields, on filtration and evaporation, hydrate of lithia.—*Hydrate of Lithia* (LiO,HO) is less soluble in water than potassa or soda; its solution has an acrid taste, and a powerful alkaline reaction. It is sparingly soluble in alcohol. It does not deliquesce by exposure, but absorbs carbonic acid and becomes opaque. At a high temperature it attacks platinum in its pure and carbonated state, and hence must be fused in a silver crucible.—*Chloride of Lithium* ($LiCl$) differs from the chlorides of potassium and sodium, in being very deliquescent and soluble in absolute alcohol; it being decomposed when strongly heated in the open air; when it loses chlorine, absorbs oxygen, and becomes alkaline; it being with difficulty crystallizable, and in tinging the flame of alcohol of a crimson-red color.—*Nitrate of Lithia* (LiO,NO_5) is a very soluble and deliquescent salt: it crystallizes in rhombic and acicular prisms, and is dissolved by alcohol.—*Sulphate of Lithia* (LiO,SO_3). The anhydrous salt is white and difficultly fusible, unless sulphate of lime is present, when it fuses below redness; its taste is saline, but not bitter; it crystallizes in rhombic prisms, which are slightly efflorescent and soluble in alcohol.—*Phosphate of Lithia* may be obtained by adding phosphoric acid to sulphate of lithia; no precipitate is at first formed, but upon adding excess of ammonia and warming the liquid a white insoluble phosphate of lithia falls. This property enables us to separate lithia from potassa and soda. The phosphate of lithia may be decomposed by dissolving it in acetic acid, and adding acetate of lead: acetate of lithia remains in solution. By heating this, carbonate of lithia may be procured.—*Carbonate of Lithia* (LiO,CO_2). When a strong solution of carbonate of ammonia is added to a concentrated solution of sulphate of lithia and the mixture is heated, a white precipitate of carbonate is formed. It requires at least 100 parts of water at 60° for its solution, and is insoluble in alcohol. It is fusible at a high temperature. The aqueous solution has a strong alkaline reaction. Carbonate of lithia is rendered more soluble in water by carbonic acid. Some Bohemian mineral springs contain lithia in this state. An artificial water of this description has lately been employed in medicine under the name of *Aërated lithia water.*

Tests for Lithia and its Salts.—Lithia is characterized by the splendid crimson-red color which it imparts to flame, as well as by the peculiar spectrum which the colored flame produces (p. 57.) The carbonate of lithia is less soluble in water than the carbonates of potassa and soda; but much more soluble than the carbonates of the four alkaline earths. 1. A solution of the carbonate is strongly alkaline, and gives a yellowish-white precipitate with nitrate of silver. 2. It gives a dense white precipitate with the salts of baryta, strontia, and lime, as well as with the aqueous solutions of these three alkaline earths. 3. It gives no precipitate with sulphate of magnesia until boiled; and only slowly precipitates a solution of corrosive sublimate. (In these respects it resembles the bicarbonates of potassa and soda.) A small portion of the carbonate on platinum wire imparts a crimson-red color to the flame of alcohol. A concentrated solution of lithia is precipitated by solution of ammonia; but the precipitate, which is hydrate of lithia, is redissolved when heated.

The other salts of lithia possess these general characters. 1. Carbonate of potassa will slowly give, with their solutions if concentrated, a precipitate of carbonate of lithia. The precipitation is accelerated by heat. 2. Phosphate of soda slowly precipitates them in the cold, but immediately when heated. 3. Chloride of platinum, and diluted sulphuric as well as oxalic acid, produce no change in the solution. 4. Ammonia gives no precipitate in a solution of a salt of lithia, and, when diluted, the addition of phosphate of soda causes only a slow precipitation. If the mixture is boiled, a precipitate is formed immediately. 5. The solubility of the chloride in absolute alcohol, enables a chemist to separate this base from potassa and soda. 6. The crimson-red color given to flame by all the salts, is characteristic of lithia.

CÆSIUM ($Cæ=123$).

This alkaline metal was discovered by Bunsen and Kirchoff in 1860, by a spectral analysis of the residue of the mineral water of Durckheim (p. 58). A ton of the water was estimated to yield not more than three grains of chloride of cæsium. The metal derives its name from the Latin *cæsius*, signifying grayish blue, this being the color of the two lines produced in its spectrum. It exists in small quantity in the mineral water of Kreuznach, forming not more than 1-3,000,000th part of the solid contents. Bunsen obtained about 250 grains of the platinum salt of cæsium from the residue of twenty tons of this water. The residue of 9000 gallons of the Durckheim water yielded about an ounce of the pure chloride. Cæsium was procured in the state of amalgam with mercury by the electrolysis of the fused chloride. The first step in the process was to separate from the residue of the water, the salts of all other alkalies, excepting those of potassa and soda. Chloride of platinum was then added. Compounds of potassa and cæsia ($KCl,PtCl_2,CæCl,PtCl_2$) were thrown down. The platino-chloride of potassium was separated from that of cæsium by boiling distilled water, in which the latter is but little soluble.

The metal cæsium decomposes water, setting free hydrogen, and forming a strongly alkaline solution of protoxide of cæsium ($CæO$), or cæsia. The hydrate of cæsia ($CæO,HO$) is soluble in alcohol, corrodes platinum like lithia, and is volatile at a high temperature. The *carbonate* is soluble in water and alcohol, is highly alkaline, deliquescent in air, absorbs carbonic acid, and forms a bicarbonate which crystallizes in prisms. The *nitrate* and *sulphate* are anhydrous crystalline salts, soluble in water: the latter forms an alum with sulphate of alumina. The *chloride* ($CæCl$) crystallizes in cubes, which are deliquescent, in which respect it resembles chloride of lithium, and differs from the chlorides of potassium, sodium, and rubidium. It is fusible and volatile.

Cæsium is always found associated with rubidium. It appears to be extensively diffused, but exists only in traces; and probably but for spectral analysis, it would have remained undetected. This is at present the only available method of determining its presence in the residues of water. The 1-70,000th part of a grain of cæsia may be thus detected.

RUBIDIUM ($Rb=85$).

This metal derives its name from two intensely red lines which its spectrum produces near the extreme end of the less refrangible rays. It requires about the 30,000th of a grain of the chloride to render the lines visible (*see* p. 58.) Rubidium is commonly found associated with cæsium, but it appears to be more abundant. Thus, a ton of the Durckheim water gave about four grains of chloride of rubidium. Bunsen estimates the proportion of rubidia in the Durckheim spring, at 1-2,000,000 part of the weight of the water. Sea-water contains 1-400,000, and the lepidolite of Moravia 1-2,000th of its weight of the oxide of this metal.

For the separation of the metal, about 300 pounds of lepidolite are employed in one operation. The lithia is separated by the usual process (p. 319), and the residue, concentrated by evaporation, is precipitated by chloride of platinum. The platino-chloride of potassium ($KCl,PtCl_2$) is separated by successive quantities of hot water, by which the rubidium salt, like the cæsium salt, is not readily dissolved. It requires 158 times its weight of boiling water for solution, while the potassium salt requires only 19 times its weight. (According to Bunsen, 100 parts of boiling water will dissolve 5·18 of the potassium salt, 0·634 of the rubidium salt, and 0·377 of the cæsium salt). The platino-chloride of rubidium ($RbCl,PtCl_2$) is decomposed by hydrogen, and chloride of rubidium is obtained. When the chloride is fused and submitted to electrolysis, the metal is obtained at the negative pole. Rubidium decomposes water, liberating hydrogen, and forming an oxide (RbO). It is, according to Bunsen, a powerful base, and is more electro-positive than potassium. Rubidia forms a *hydrate* soluble in water and alcohol. Like hydrate of potassa, it is fusible, and when exposed to air absorbs water and carbonic acid. The *carbonate* of rubidia (RbO,CO_3,HO) is fusible, deliquescent, and soluble in water, producing a strongly alkaline liquid. It is not soluble in absolute alcohol; and as the carbonate of cæsia is soluble in this liquid, alcohol furnishes a method of separating the two alkalies. The *sulphate* and bisulphate are similar to those of potassa. The *chloride* (Rb,Cl), like that of potassium, is colorless and crystallizes in cubes: it is fusible and volatile.

Rubidia and cæsia resemble potassa in giving precipitates with chloride of platinum, which are less soluble than the platino-chloride of potassium. They also give crystalline precipitates with tartaric acid, and uncrystalline precipitates with fluosilicic acid. These new alkalies are therefore liable to be mistaken for potassa. Irrespective of the difference in the solubility of the chlorides, the only certain method of distinguishing them is that by which they were discovered, namely, spectral analysis.

Rubidium and cæsium have been found in nearly all mineral waters abounding in salts of potassa, soda, and lime, and only in infinitesimal quantities.

CHAPTER XXVI.

BARIUM, STRONTIUM, CALCIUM, MAGNESIUM.

BARIUM ($Ba=69$).

THIS metal was discovered in 1808 by Davy, who obtained it by electric decomposition of its oxide. It may also be procured by passing potassium in vapor over baryta heated to redness in an iron tube. Barium is of a gray color, and rapidly absorbs oxygen; when gently heated, it burns with a red light. It is not fusible at the melting point of glass. Its sp. gr. is 1·5 (PELOUZE). It decomposes water, evolving hydrogen, and forming a solution of baryta; its properties, however, have not been accurately ascertained.

Oxide of Barium; Baryta (BaO) is obtained by exposing pure *nitrate of baryta* to a bright red heat in a porcelain crucible; it acts upon platinum, and if a silver crucible be employed, the heat required is such as to endanger its fusion. Baryta may also be obtained by subjecting artificial *carbonate of baryta* to an intense white heat, thoroughly mixed with about 10 per cent. of finely-powdered charcoal. Baryta is generally in the form of a porous mass, or gray powder, and when pure, is very difficult of fusion. Its specific gravity is about 4, hence the name *Baryta,* as being the *heaviest* of the substances usually called *earths* (from βαρὺς, *heavy*). It is very poisonous. It has a strong alkaline taste, and reaction on vegetable colors. It is insoluble in alcohol. It eagerly absorbs water, heat is evolved, and a white hydrate is formed. After long exposure to air it becomes white, and is a mixture of the hydrate and carbonate.

Hydrate of Baryta (BaO,HO).—When pure baryta is sprinkled with water it becomes intensely hot, and crumbles into a bulky white powder, which fuses, but does not give out water at a red heat. It dissolves in 20 parts of cold, and in 3 of boiling water, forming a solution which is a very delicate test of the presence of carbonic acid, and which speedily becomes covered with a film of carbonate of baryta when exposed to air. A saturated solution of baryta in hot water deposits hexagonal prisms as it cools, containing 10 equivalents of water.

Peroxide of Barium (BaO_2) is obtained when dry oxygen gas is passed over baryta heated to dull redness in a glass or porcelain tube: it may also be formed by adding 1 part of chlorate of potassa to 4 of baryta, previously heated to redness in a platinum crucible; the oxygen of the chlorate combines with the baryta, and, by the action of cold water, the remaining chloride of potassium may be washed out, and a *hydrated peroxide of barium* remains. When the anhydrous peroxide, which is of a gray color, is put into cold water, it does not evolve heat, but becomes a white, pulverulent, and insoluble hydrate ($BaO_2,6HO$); but if this is boiled in water, it will give out an equivalent of oxygen, and revert to the state of protoxide, which is soluble. When peroxide of barium is heated in hydrogen it becomes incandescent, emitting a greenish flame, and absorbing the gas; protohydrate of baryta is the product. Peroxide of barium is also formed when dry air is passed over heated baryta: the temperature required for this absorption of oxygen is a dull red heat: at a bright red heat not only is no oxygen absorbed, but the peroxide is itself decomposed, and giving off 1 atom of oxygen, reverts to the state of protoxide, which may thus be used to absorb and evolve oxygen by turns: this has been proposed as an economical source of oxygen, but independently of the difficulty in the due adjustment of the heat, the capacity of baryta for absorbing oxygen gradually decreases by repeated use (p. 83).

Nitrate of Baryta (BaO,NO_5) may be produced by dissolving the native carbonate in dilute nitric acid, evaporating to dryness, redissolving and crystallizing; or by decomposing a solution of sulphide of barium by dilute nitric acid. It forms permanent octahedral crystals, which are anhydrous, and taste acrid and astringent. It is soluble in 12 parts of cold and 4 of boiling water. It is insoluble in alcohol. If a moderately strong solution of nitrate of baryta is added to nitric acid, a precipitation of the nitrate of baryta takes place, in consequence of the difficult solubility of the nitrate in the dilute acid; in the concentrated acid the nitrate is insoluble; hence, in using nitrate of baryta as a test of the presence of sulphuric acid in nitric acid, the latter should be considerably diluted, lest the precipitated nitrate of baryta be mistaken for sulphate.

Chloride of Barium (BaCl).—This compound may be obtained by heating baryta in chlorine (in which case oxygen is evolved, to the amount of half a volume for every volume of chlorine absorbed); or in hydrochloric acid gas, when it becomes red hot, and chloride of barium and water are the results. It is generally formed by dissolving carbonate of baryta in diluted hydrochloric acid, evaporating to dryness, and fusing the residue in a covered platinum crucible. Chloride of barium, after it has been thus fused, is translucent and of a grayish color; sp. gr. 3·8; its taste is acrid; it is not deliquescent, but absorbs moisture and becomes opaque, increasing in weight after a few days to the amount of 13 to 14 per cent.; when moistened it evolves heat: 100 parts of water at 32° dissolve between 32 and 33 parts of this anhydrous chloride: it is insoluble in absolute alcohol, but imparts a pale greenish-yellow color to its flame during combustion. Its aqueous solution yields, when evaporated, flat four-sided crystals$=$BaCl,2HO, which effloresce in dry air. At 212° the water is expelled, and anhydrous chloride remains. 100 parts of water at 60° dissolve about 43 parts of these crystals.

Sulphide of Barium (BaS) is formed, 1. By passing sulphuretted hydrogen over red-hot baryta in a coated glass or porcelain tube, as long as water is formed; it yields a gray granular compound: $BaO+HS=BaS+HO$. 2. By passing hydrogen over finely-powdered sulphate of baryta at a bright red heat: $BaO,SO_3+4H=BaS+4HO$. 3. By the action of charcoal upon ignited sulphate of baryta; $BaO,SO_3+4C=BaS+4CO$. Mix sulphate of baryta, in fine powder, into a paste, with an equal volume of flour, place it in a covered crucible, and expose it to a white heat for an hour or two. On pouring hot water on the product, the sulphide of barium is dissolved, and may be separated from undecomposed sulphate and excess of charcoal, by filtration.

Sulphide of barium is readily soluble in hot water, and the solution on cooling out of the contact of air, deposits hydrated crystals. By exposure to air, it absorbs carbonic acid and oxygen, yielding carbonate and hyposulphite of baryta. It dissolves sulphur, forming a *pentasulphide*. When its solution is boiled with oxide of copper till it ceases to blacken acetate of lead, and filtered whilst hot, it yields on evaporation, pure baryta.

Sulphate of Baryta (BaO,SO_3) is an abundant natural product known under the name of *heavy spar;* it is insoluble in water, hence the solutions of baryta are accurate tests of the presence of sulphuric acid and the soluble sulphates.

Recently precipitated sulphate of baryta is sometimes very obstinate in subsiding from water, and not only long remains suspended, but adheres to the glass, and even passes through filtering-paper: heat, and a little excess of acid, greatly facilitate its deposition. It may be heated to redness without change, and hence the filter containing it, in some cases of quantitative analysis, may be conveniently burned away; but the carbon of the paper converts a minute portion of the sulphate into sulphide. 100 grains of the incinerated sulphate correspond to 65·63 grains of baryta.

Carbonate of Baryta (BaO,CO_2).—This salt falls in the form of a white powder, when the soluble salts of baryta are precipitated by carbonate of ammonia. It is so nearly insoluble, that water at 60° only takes up about 1-4300th part. Water saturated with carbonic acid dissolves 1-820th. It has no alkaline reaction on vegetable colors.

Native Carbonate of Baryta, or *Witherite,* is found crystalline and massive. Its density is 4·33. It is useful as a source of pure baryta and its salts. Though scarcely soluble in water, it is poisonous, probably in consequence of its solubility in the acids of the stomach. It dissolves more sparingly in solution of carbonic acid than the precipitated carbonate, and is more difficultly decomposed.

TESTS FOR BARYTA AND ITS SALTS.—A solution of *baryta* has an alkaline reaction: and it gives a brown precipitate with nitrate of silver. It differs from the solutions of potassa and soda in acquiring a white incrustation (carbonate of baryta) on exposure to air. It is immediately precipitated as a white carbonate, by a current of carbonic acid, or by the addition of a few drops of a solution of carbonate or bicarbonate of potassa, soda, or ammonia.

There are two *soluble* barytic salts, the nitrate and the chloride. They are characterized by the following properties: 1. The solution is neutral; 2. It gives a white precipitate with alkaline carbonates and bicarbonates; 3. It is precipitated white by sulphuric acid and all soluble sulphates, even by the sulphates of lime and strontia. This precipitate, sulphate of baryta, is insoluble in diluted acids and alkalies; 4. It gives a white precipitate with fluosilicic acid; and 5. A white precipitate with an alkaline hyposulphite; 6. It gives a yellowish-white precipitate with a solution of chromate of potassa; 7. Oxalic acid does not precipitate the solution of either of these salts unless they are highly concentrated, and then after a time a crystalline precipitate of binoxalate of baryta may be formed; 8. When a small portion of the salt is introduced into the flame of alcohol, it produces a pale greenish-yellow color, which when viewed through a solution of indigo, appears bluish green. The spectrum produced by this flame presents a variety of well-marked colors (p. 58), and is distinguished from all, excepting that of calcium, by numerous green bands.

In reference to the *insoluble* salts, the carbonate may be dissolved by nitric acid, and the sulphate converted into sulphide (p. 323), and this compound into chloride by hydrochloric acid. They may then be tested.

STRONTIUM ($Sr=44$).

Strontia was first discovered in the state of *carbonate* at Strontian in Argyleshire, and was supposed to be a carbonate of baryta: it was first shown to contain a peculiar earth by Dr. Hope, in 1792. It is a substance of rare occurrence. The existence of *strontium*, as the metallic base of the earth, was first demonstrated by Davy in 1808. It is a fixed metal of a gray color with a reddish reflection. It has been recently obtained, but in small quantities, by Bunsen and Matthiessen. The fused chloride was decomposed by electrolysis, iron being employed for the poles of the battery. The strontium which adhered to this metal was removed, and preserved in naphtha, in which it could be moulded. It was rapidly oxidized on exposure to air; it decomposed water without combustion, setting free hydrogen, and forming a soluble protoxide. The metal has a sp. gr. of 2·5, it therefore sinks in water.

PROTOXIDE OF STRONTIUM. STRONTIA (SrO) may be obtained from the nitrate, the carbonate, and the sulphate of strontia, by processes similar to those directed in regard to baryta. It is a grayish-white porous substance: its specific gravity is 3·9; it is extremely infusible, not volatile, has an acrid taste, and an alkaline reaction.

HYDRATE OF STRONTIA (SrO,HO).—When strontia is sprinkled with water it heats and falls to powder, forming a white hydrate, which, when subjected for a long time to a high temperature, gradually becomes anhydrous. It is insoluble in alcohol. It dissolves in about 160 parts of water at 60°. Boiling water dissolves it more abundantly, and on cooling deposits crystals containing 10HO.

NITRATE OF STRONTIA (SrO,NO_5) is obtained by processes similar to those for obtaining *nitrate of baryta:* it crystallizes in octahedra, soluble in 5 parts of water at 60°, and in half its weight of boiling water. It is insoluble in anhydrous alcohol. Its taste is pungent and cooling. At a red heat the acid is evolved and decomposed, and strontia remains. It is used in the *red fire* employed at the theatres, which consists of 40 parts of fused nitrate of strontia, 13 of powdered sulphur, 5 of chlorate of potassa, and 4 of sulphide of antimony. The chlorate and sulphide should be separately powdered and cautiously mixed with the other ingredients. When nitrate of strontia is finely powdered and mixed with alcohol, it communicates a beautiful red tint to the flame.

CHLORIDE OF STRONTIUM ($SrCl$) is obtained by dissolving *carbonate of strontia* in hydrochloric acid, evaporating to dryness, and fusing the residue. It is of a gray color and an acrid taste; its sp. gr. is 2·8. The aqueous solution of the chloride when concentrated furnishes white prismatic crystals, which are deliquescent. The chloride is soluble in alcohol. These properties enable a chemist to distinguish baryta from strontia, and to separate the two bases when in the state of chloride. Chloride of barium crystallizes in quadrangular plates, which are not deliquescent, and are insoluble in alcohol.

SULPHATE OF STRONTIA (SrO,SO_3) is of very sparing solubility, 1 part requiring 3600 of water. It is distinguished from sulphate of baryta by being slowly soluble in solution of chloride of sodium. It is insoluble in solution of sal-ammoniac. It is soluble in boiling sulphuric acid, but falls upon dilution. When heated with charcoal, its acid is decomposed, and *sulphide of strontium* formed. *Native Sulphate of Strontia* is sometimes of a blue tint, and has hence been called *cœlestine.* The finest crystallized specimens are accompanied with native sulphur, from Sicily.

CARBONATE OF STRONTIA (SrO,CO_2), when artificially formed is a white powder, soluble in 1536 parts of hot water. *Native Carbonate of Strontia,* or *Strontianite,* is a rare mineral. It has a greenish tint, and occurs in radiated masses, and sometimes in acicular and hexahedral crystals.

TESTS FOR STRONTIA AND ITS SALTS.—A solution of *strontia* resembles that of baryta in alkaline reaction—in giving a brown precipitate with nitrate of silver, and producing a white incrustation of carbonate by exposure to air, or on the addition of a solution of an alkaline carbonate. The solutions of baryta and strontia may be thus distinguished: 1. Sulphuric acid gives a white precipitate, immediately with baryta, slowly with strontia. 2. Sulphate of lime precipitates baryta, but not strontia. 3. Fluosilicic acid precipitates baryta, but not strontia. 4. Oxalic acid precipitates both; a slight excess of the acid will redissolve oxalate of baryta, but oxalate of strontia is insoluble in the acid.

The principal *soluble salts* are the nitrate and chloride. They are neutral. Like those of baryta, they are precipitated white by alkaline carbonates and bicarbonates. The differences are: 1. Sulphuric acid and alkaline sulphates precipitate strontia slowly, but baryta immediately. 2. Sulphate of strontia produces no precipitate in them. 3. Fluosilicic acid precipitates a concentrated solution of a salt of strontia very slowly. 4. An alkaline hyposulphite does not give a precipitate with a salt of strontia. 5. Oxalic acid produces slowly a white granular precipitate. 6. A salt of strontia gives to the flame of alcohol a rich red color, which traverses a stratum of solution of indigo, and appears of a deep crimson tint. By spectral analysis this color is resolved into eight lines or bands—red, orange, and blue, but there are no green lines (p. 57).

CALCIUM (Ca=20).

The existence of *calcium*, as the metallic base of lime, was first demonstrated by Davy in 1808. Like strontium, calcium has been obtained by the electrolysis of its chloride, iron poles being employed with the battery. (BUNSEN.) This metal has a yellowish color, is harder than lead, malleable, fusible at a red heat, but not volatile, and is only slowly oxidized when exposed to humid air. It burns with scintillations into quicklime when heated in the air, and it undergoes vivid combustion in chlorine, and in the vapor of bromine, iodine, and sulphur. Its specific gravity is 1·57; it sinks in water, and rapidly decomposes it without combustion, hydrogen being liberated, and lime (protoxide of calcium) being dissolved by the water.

OXIDE OF CALCIUM; LIME; *Quicklime* (CaO).—Lime may be obtained in a state of considerable purity by exposing humid carbonate, or nitrate of lime, to a white heat for an hour, in an open crucible (p. 130). Pure lime is white, acrid, caustic, and alkaline; its specific gravity is 3·08. It is infusible, but remarkably promotes the fusion of some other oxides, and is, therefore, used in several metallurgic processes, as a flux. When intensely heated, as, for instance, by the oxyhydrogen blowpipe, it is remarkable for its luminosity, and at this very high temperature a minute quantity is volatilized (p. 113). It is an essential ingredient in mortar and other cements. Exposed to air, it absorbs water and then carbonic acid, and, losing its causticity, becomes partially converted into carbonate of lime; so that when used for agricultural purposes, it should, generally speaking, be speedily ploughed in, and not left in heaps upon the surface so as to acquire carbonic acid. In its caustic state, it is most active in the destruction of vermin, and in effecting chemical changes upon the organic and inorganic constituents of the soil. Its powerful affinity for water renders it useful in various cases of dehydration, as in drying certain gases, and abstracting water from alcohol and some other liquids; in the state of hydrate, or diffused through water (cream and milk of lime), it is also used as an absorbent of carbonic acid; when perfectly dry it does not absorb that gas.

Lime-burning.—Although all carbonates of lime may, by burning, be brought to the state of quicklime, chalk and *compact* limestone are alone used for this purpose in the large way. The limekiln at present almost universally employed in this country, is a cup-shaped concavity, in a solid mass of masonry, open at top and terminated at bottom by a grate, immediately above which is an iron door. This simple furnace is first charged with fuel (either wood, or coal and cinders), upon which is afterwards laid a stratum about a foot thick, of chalk or limestone, broken into pieces not larger than the fist; to this succeeds a charge of fuel, and so on alternately, keeping the kiln always full. The pieces of limestone descend towards the bottom of the kiln in proportion as the fuel is consumed, being in the meantime kept at a pretty full red heat. At this temperature the water and carbonic acid are driven off; and by the time the limestone arrives at the bottom of the kiln, which happens in about forty-eight hours, it is rendered perfectly caustic. The door above the grate is then opened, and the lime below the next descending stratum of fuel is raked out; the remaining contents of the furnace sink down, and a fresh charge is laid on the top. The compact limestone, after having undergone this process, though lighter and more porous than before, still retains its figure unaltered; hence it is readily separable from the ashes of the fuel, and is sufficiently hard to be carried from place to place without falling to pieces.

Attempts have been made to burn lime, or, in other words, to expel the carbonic acid from limestone, in close vessels, but the carbonic acid cannot be so driven off (p. 130).

HYDRATE OF LIME; SLAKED LIME; (CaO,HO).—When a small quantity of water is poured upon lime, a rise of temperature ensues from the solidification and combination of a portion of the water, and a bulky white powder is obtained, which is a *hydrate.* The rise of temperature is so great, when large heaps of good lime are suddenly slaked, as to scorch wood (p. 133). Hydrate of lime may be obtained in a crystalline form, by placing lime-water under the receiver of an air-pump, containing another vessel of sulphuric acid. The water is thus slowly evaporated, and six-sided crystals (CaO,HO) are formed.

Lime-water.—At a temperature of 60°, 750 parts of water are required for the solution of one part of lime. Boiling water, however, does not dissolve so large a quantity; 1 part of lime requiring 1280 parts of water at 212° for its solution; at 32°, 1 part of lime is soluble in 656 of water. When lime-water is boiled, a portion of the lime is therefore precipitated in small crystalline grains.

Lime-water is limpid and colorless; its taste is nauseous and alkaline, and although the quantity of lime which it contains is relatively small, its alkaline reaction is very marked. It is usually prepared by pouring warm water upon powdered lime, and allowing the mixture to cool in a close vessel; the clear part is then decanted from the remaining undissolved portion. When lime-water is exposed to the air, a pellicle of carbonate of lime forms upon its surface, which, if broken, is succeeded by others, until the whole of the lime is thus separated.

CHLORIDE OF CALCIUM; MURIATE OF LIME; ($CaCl$).—This compound occurs in sea-water and in some saline springs, where it is sometimes accompanied by traces of bromine and of iodine. It is formed by dissolving carbonate of lime in hydrochloric acid, evaporating to dryness, and exposing the residue to a red heat in close vessels. It soon deliquesces when exposed to air, and is frequently employed, after it has been fused, to deprive gases of aqueous vapor; but when thus used, its absorptive powers in regard to some gases must not be overlooked. It is also used as a means of depriving alcohol, ether, and other liquids, of water, for which purpose they are generally distilled off dry chloride of calcium. Its taste is bitter and acrid. One part of water at 66° dissolves four parts of this chloride; its solubility, however, is greatly influenced by temperature, for at 32° one part of water will not dissolve more than two of the salt, and at 212° it takes up nearly any quantity. It is copiously soluble in alcohol, and heat is evolved during the solution, which in cold weather affords crystals containing about 60 per cent. of alcohol, instead of water of crystallization. By the solubility of this chloride in alcohol, lime may be separated from potassa, soda, and baryta. It is produced in the manufacture of carbonate of ammonia, from the decomposition of hydrochlorate of ammonia by lime, and hence it was formerly called *fixed sal-ammoniac.*

Hydrated Chloride of Calcium is obtained by evaporating the aqueous solution to the consistence of a thick syrup; on cooling, it concretes into a crystalline mass, which is $CaCl,2HO$. By exposing a strong aqueous solution of chloride of calcium to a temperature of 32°, it yields striated four-sided prisms$=CaCl,6HO$.

CHLORIDE OF LIME; *Hypochlorite of Lime.*—This important bleaching material is made by passing chlorine into chambers containing hydrate of lime in fine powder, by which the gas is copiously absorbed. It is a dry white powder, smelling feebly of chlorine, and having an acrid taste; it is partially soluble in water, and the solution is used under the name of *bleaching-liquor.* Exposed to air, it slowly evolves chlorine and absorbs carbonic acid; ultimately some chloride of calcium is formed, and it deliquesces. When heated, it gives off oxygen, and chloride of calcium results, an experiment which shows the superior attraction of calcium for chlorine as compared with oxygen, the latter being expelled from the lime.

The solution obtained by digesting bleaching-powder in distilled water has a strong alkaline reaction upon most of the usual tests, and its bleaching power is only slowly developed unless some acid is added, when it is powerful and immediate; thus it is that calico-printers produce white figures upon colored ground, by printing the pattern intended to be brought out upon the colored calico, in citric or tartaric acid thickened with starch or gum; the goods are then rapidly wound through a properly-adjusted solution of chloride of lime, and the bleaching power only shows itself where the acid pattern had been previously applied. In the same way a solution of the chloride may be colored blue by litmus, or green by red cabbage, or brown by turmeric, and on the addition of a few drops of acid the color disappears. By exposure to air, the absorption of carbonic acid effects the same change; and the evolution of that acid in respiration is well shown, by tinging a weak solution of chloride of lime blue by litmus, and then breathing through it by means of a tube, when the blue color gradually disappears.

The best samples of commercial chloride of lime contain on an average about 30 per cent. of chlorine; and when chlorine is passed over hydrate of lime in an experiment upon the small scale, it cannot be made to absorb more than about 40 per cent.; but if hydrate of lime be diffused through water, it will absorb its own weight of chlorine, and a solution containing 1 equivalent of lime (or of hydrate of lime) and 1 of chlorine (which is the true atomic compound) is obtained. In its ordinary state, bleaching-powder may be regarded as containing:—

Chlorine	1	36	32·72
Hydrate of lime	2	74	67·28
Bleaching-powder . . .	1	110	100·00

When put into water, 1 atom of hydrate of lime remains undissolved, and the solution contains 1 atom of lime and 1 of chlorine (p. 177). Some have considered bleaching-powder as containing a *hyperchlorite of lime,* and represent its formation as follows: $2CaO + 2Cl = CaCl + CaO,ClO$. But when properly prepared, it yields no chloride of calcium when digested in alcohol, and it is not deliquescent. When used as a *bleaching agent* for calico, the goods are in the first instance washed, and then boiled in a weak solution of soda to cleanse them of greasy and other impurities; they are then put into a weak solution of the chloride of lime, and then into water slightly acidulated by sulphuric acid. These operations are repeated if necessary, and the process is completed by thoroughly washing the goods in running water. When employed as a *disinfectant,* cloths soaked in a solution of the chloride are suspended in the apartments, where they slowly evolve chlorine in consequence of the action of the carbonic acid of the air. Or, if a larger and more sudden evolution of chlorine is required, dilute sulphuric acid is added to the powder or its solution.

The *quality* of chloride of lime may be determined either by testing its bleaching power by means of a standard solution of indigo, or by determining the quantity of protoxide of iron in acid solution, which is convertible into peroxide by a given weight of the powder; in this case, supposing protosulphate of iron to be used, *one* equivalent of chlorine will convert *two* equivalents of that salt into one of persulphate of iron. (GRAHAM.)

FLUORIDE OF CALCIUM; FLUOR-SPAR (CaF).—This compound may be produced by saturating dilute hydrofluoric acid with carbonate of lime, or by precipitating a neutral salt of lime with a soluble fluoride: in this case it forms a gelatinous mass, the precipitation of which is accelerated by the addition of caustic ammonia. *Native fluoride of calcium*, or *fluor-spar*, is a mineral found in many parts of the world, but in great beauty and abundance in England, and especially in Derbyshire, where it is commonly called *blue John*. It occurs in cubic crystals, which may be cleaved into octahedra and tetrahedra. Its colors are various. Its specific gravity=3. It phosphoresces when exposed to heat, and at a high red heat it fuses, and is sometimes used as a flux for promoting the fusion of other minerals. It generally occurs in veins; in the Odin mine at Castleton, it is found in detached masses, from an inch to more than a foot in diameter; their structure is divergent, and the colors, which are various, disposed in concentric bands. It is the only variety which admits of being turned in the lathe into vases and other ornamental articles. *Compact fluor* is a scarce variety; the finest specimens come from the Hartz. A third variety is *chlorophane*, so called from the beautiful pale-green light which it exhibits when heated. The nature of the coloring-matter of blue and green fluor-spar is not understood: it is liable to fade, and the blue varieties become red and brown by heat. Fluoride of calcium exists in small quantity in bone: it has been found in coprolites, and in some fossil bones, to the extent of 10 per cent. Pure fluoride of calcium is slowly decomposed by cold sulphuric acid, forming with it a viscid mixture. At a temperature of about 100° its decomposition is rapid, sulphate of lime is formed, and hydrofluoric acid is evolved. If the fluor-spar contain silica, sulphuric acid immediately acts upon it, evolving white fumes of silicofluoric acid. Fused with carbonate of potassa, carbonate of lime and fluoride of potassium are produced.

NITRATE OF LIME (CaO,NO_5).—This is a deliquescent salt soluble in one-fourth its weight of water at 60°. It is found in old plaster and mortar, from the washing of which nitre is procured by the addition of carbonate of potassa. It sometimes occurs in spring and river water. It may be crystallized by very low evaporation. It is soluble in alcohol. When exposed to heat it fuses, and on cooling concretes into a phosphorescent substance called *Balduin's phosphorus*. At high temperatures the acid is driven off, and pure lime remains.

SULPHIDE OF CALCIUM (CaS) is formed by passing sulphuretted hydrogen over red-hot lime, when water is evolved: $CaO+HS=CaS+HO$. It is also formed by the action of charcoal, or of hydrogen, upon *sulphate of lime* at a red heat. It is slowly acted upon by water, forming a colorless solution. When freshly prepared it is phosphorescent (*Canton's phosphorus*.)

BISULPHIDE OF CALCIUM (CaS_2).—When sulphur and hydrate of lime, about equal weights, are boiled together in water, and the solution cooled, yellow prismatic crystals form, which, after having being dried *in vacuo*, are permanent: their taste is alkaline and sulphurous; they contain 1 atom of calcium, 2 of sulphur, and 3 of water: when gently heated *in vacuo* they become anhydrous, and the bisulphide remains. The yellow liquor, from which the crystals are deposited, retains hyposulphite of lime in solution: $6S+3CaO=CaO,S_2O_2+2CaS_2$. By exposure to air it becomes colorless, in consequence of its conversion into hyposulphite.

PENTASULPHIDE OF CALCIUM (CaS_5).—When excess of sulphur is boiled in water with quicklime, a compound of 5 atoms of sulphur with 1 of calcium is formed, which is not crystallizable: it is soluble in alcohol; and when its aqueous solution is evaporated *in vacuo*, it leaves a yellow mass containing about 80 per cent. of sulphur. By heat it loses sulphur, and becomes protosulphide.

HYPOSULPHITE OF LIME (CaO,S_2O_2).—When crystals of hydrated bisulphide of calcium are ground in a mortar with sulphurous acid, it loses its odor, and when filtered it is found to be a solution of *hyposulphite of lime*. By passing sulphurous acid through the yellow liquor obtained by boiling lime and sulphur in water, the same product is obtained; and if the solution be filtered and evaporated, at a temperature not exceeding 140°, it furnishes hexagonal crystals ($=CaO,S_2O_2,+6HO$), which at the temperature of ebullition are decomposed into sulphite of lime and sulphur. The crystals are little altered by air, very soluble in water, and insoluble in alcohol. This salt is occasionally employed in photography as a means of removing the salts of silver from drawings, so as to render them permanent when exposed to light.

SULPHITE OF LIME (CaO,SO_2) is formed by passing sulphurous acid into a mixture of lime and warm water. It is a white powder of a slightly sulphurous taste; it requires about 800 parts of water at 60° for solution: it is rendered soluble by excess of sulphurous acid, and then separates in hexangular prisms, of difficult solubility, efflorescent, and passing into sulphate of lime by exposure to air.

SULPHATE OF LIME (CaO,SO_3) occurs native in *selenite*, *gypsum*, and *plaster-stone*. It is formed artificially by decomposing a solution of a soluble salt of lime, by sulphuric acid or by a soluble sulphate. When slowly deposited, it forms silky crystals soluble in 350 parts of water. When these, or the *native crystallized sulphate* ($CaO,SO_3 2HO$), are exposed to a heat of about 300°, they lose 20 per cent. of water, and fall into a white powder (*plaster of Paris*), which, made into a paste with water, soon solidifies, and when in large quantity, with very sensible increase of temperature: hence its use in taking casts for busts, figures, and ornaments; it is also the basis of stucco, and scagliola or artificial marble, which is made by mixing plaster of Paris, colored in various ways, with size and water; when it has indurated, its surface is polished. Exposed to a red heat, but short of its fusing-point, it loses this property of recombining with water. The sp. gr. of anhydrous sulphate of lime (artificial) is 2·927: it requires about 500 parts of water at 60°, and 450 parts at 212°, for its solution. Like other sulphuric salts, it is slowly decomposed when its solution is subjected to the action of decaying vegetable matter, in which case the odor of sulphuretted hydrogen becomes apparent. As sulphate of lime is more soluble in water than pure lime, sulphuric acid affords no precipitate when added to *lime-water*. Nearly all spring and river waters contain traces of this salt, and in those waters which are called *hard* it is often abundant; it renders them unfit for washing and for culinary purposes. At a very high temperature sulphate of lime is fusible, but suffers no decomposition; heated with charcoal it is converted into sulphide of calcium. It dissolves in dilute nitric and hydrochloric acids, and separates from these solutions silky crystals. It is decomposed by the alkaline carbonates. Sulphate of lime is sometimes employed as a manure, and, when sprinkled over the land in small quantity, is said to improve certain soils, especially for the growth of clover: is used for many purposes in the arts.

Native Sulphate of Lime occurs in various forms. The *crystallized* or *hydrous* variety, $CaO,SO_3,2HO$, is called *selenite;* the fibrous and earthy, *gypsum;* and the granular or massive, *alabaster*. The primitive form of selenite is a rhomboidal prism. The crystals are commonly transparent, of a specific gravity of 2·32, and may be scratched by the nail. A beautiful fibrous variety, called *satin gypsum*, is found in Derbyshire, applicable to ornamental purposes. *Massive and granular gypsum* is found in the sandstone accompanying the salt-deposits in Cheshire. It abounds in the strata of Montmartre, near Paris. In the Tyrolese, Swiss, and Italian Alps, it is found upon the primitive rocks. It is turned in the lathe, and sculptured into a variety of beautiful forms. There is a variety of sulphate of lime which has been called *anhydrous gypsum* or *anhydrite*, in reference to its containing no water. It is harder and denser than selenite, its specific gravity being 2·96: it sometimes contains common salt, and is then called *muriacite*. It is rarely crystallized. It has been found in Derbyshire and Nottinghamshire, of a pale-blue tint; sometimes it is pink or reddish, and often white. A compound of sulphate of lime and sulphate of soda is found in the salt mines of New Castile, which mineralogists have described under the name of *Glauberite*, and which may be formed artificially by fusing the two salts.

PHOSPHIDE OF CALCIUM (CaP).—By passing the vapor of phosphorus over lime heated to dull redness, a brown compound is produced, which decomposes water with the evolution of phosphuretted hydrogen, and consists of the phosphide of calcium and phosphate of lime; the oxygen of the lime at this temperature converts a portion of the phosphorus into phosphoric acid, and the evolved calcium combines with another portion of phosphorus to form phosphide. In a damp atmosphere this substance crumbles into a brown powder, and in this state does not produce a spontaneously inflammable gas when put into water. It is rapidly decomposed by the dilute acids. (*See* PHOSPHIDES OF HYDROGEN, p. 228.)

HYPOPHOSPHITE OF LIME (CaO,PO,2HO) may be obtained by carefully boiling phosphorus in a thin cream of lime, filtering the solution, and passing carbonic acid through it, to separate excess of lime. It is also formed by the action of boiling water on phosphide of calcium, and treating the clear liquor in the same way. The solution evaporated *in vacuo*, furnishes rectangular prismatic crystals of the hypophosphite, which are nearly equally soluble in hot and cold water, and quite insoluble in alcohol: they contain from 18 to 22 per cent. of water of crystallization. This salt is used in medicine.

PHOSPHATES OF LIME.—There appears to be several definite combinations of lime with phosphoric acid, but the following is the most important.

COMMON PHOSPHATE OF LIME; TRIBASIC PHOSPHATE OF LIME; BONE PHOSPHATE; $(3(CaO),PO_5)$.—This salt occurs abundantly in bone-ash, and is found as a mineral product. On adding chloride of calcium to the tribasic phosphate of soda, a corresponding phosphate of lime precipitates. When a solution of bone-earth in hydrochloric or nitric acid is boiled to expel all carbonic acid, and decomposed by caustic ammonia, the bone-phosphate separates in the form of a bulky precipitate, which, when perfectly dried, is white and amorphous. When bone-phosphate is digested in dilute sulphuric acid, it is resolved into sulphate of lime and (if a sufficiency of sulphuric acid be used) phosphoric acid: $3(CaO),PO_5+3SO_3=3[CaO,SO_3]+PO_5$. If less sulphuric acid be used, an acid phosphate of lime is formed. Hydrochloric and nitric acids readily dissolve bone-phosphate. Acetic acid, and water saturated with carbonic acid, also dissolve it. Caustic ammonia added to these acid solutions throws down the original phosphate. It is also slightly soluble in solutions of ammoniacal salts, and of chloride of sodium; and when recently precipitated, it is slightly soluble in water. Water containing starch or gelatine in solution, dissolves it somewhat more freely.

Native phosphate of lime (bone phosphate) occurs in *apatite*, *moroxite*, *phosphorite*, and *asparagus stone;* its primitive form is a six-sided prism: it also occurs in some volcanic products. Crystallized apatite is found of great beauty in Cornwall and Devon, and the massive varieties in Bohemia and in Spain. This is one of the most beautiful of the phosphorescent minerals. When fragments of it are placed upon iron heated just below redness, they emit a brilliant pale green light. In these minerals the phosphate is generally associated with fluoride of calcium, the formula of apatite being $3[3CaO,PO_5]+CaF$. The substances known under the name of *coprolites*, and which appear to be the excrements of fossil reptiles, also abound in phosphate of lime. On the shore at Lyme Regis, and in the lias of the estuary of the Severn, they are singularly abundant. They occur throughout the lias of England, and in strata of all ages that contain the remains of carnivorous reptiles; in external form they resemble oblong pebbles, varying in size with the cells of the intestines which have produced them. Phosphate of lime occurs in small quantities in some varieties of chalk, and in certain schists and other rocks. It is present in all fertile soils, and in the vegetables they produce, through which it is conveyed to the animals that feed upon them. These facts bear importantly upon agriculture, and give great interest to the economy of bone-manure, and other sources of the phosphates. Minute quantities of phosphate of lime and phosphate of iron have been detected in the water of the deep wells of London.

CARBONATE OF LIME (CaO,CO_2) is the most abundant compound of this alkaline earth; it exists in river and spring water, and consequently in the ocean, and is an essential ingredient in fertile soils. When lime-water is exposed to air, it becomes gradually covered with an insoluble film of carbonate of lime; hence its use as a test of the presence of carbonic acid; but excess of carbonic acid redissolves it, producing a supercarbonate. It follows, therefore, that if lime-water be added, in equivalent proportion, to water holding carbonate of lime in solution by excess of carbonic acid, the whole of the lime may be thrown down in the form of an insoluble carbonate, and the water will remain pure. Carbonate of lime is also precipitated by the carbonated alkalies, from solutions of calcareous salts. It is a tasteless white powder, insoluble in pure water, and having no alkaline reaction. Exposed for a sufficient time, in a humid state, to the joint action of a red heat and current of air, the whole of the carbonic acid escapes, to the amount of 44 per cent., and quicklime is obtained. *Cream of lime* gradually absorbs carbonic acid to the amount of half an equivalent when exposed to the air, and forms a definite compound of hydrate and carbonate. It also appears, that in burning lime, one-half of the carbonic acid escapes more easily than the other, indicating the existence of a dicarbonate$=2(CaO),CO_2$.

Native Carbonate of lime occurs in great abundance and in various forms. The primitive form of the crystallized carbonate or *calcareous spar*, is an obtuse rhomboid. Its specific gravity is 2·72. It occurs in every kind of rock, and its secondary forms are more numerous than those of any other substance. What is termed *Iceland spar* is this substance in its primitive form, and of extreme purity; it is highly doubly refractive when transparent. Some of the varieties are opaque or translucent, snow-white, or tinged of different hues. It is recognized by its rhomboidal fracture and moderate hardness, being scratched by fluor-spar; before the blowpipe it loses carbonic acid, and becoming *lime*, is intensely luminous. Carbonate of lime sometimes forms *stalactites* and *stalagmites*, of which some of the caverns of Derbyshire furnish magnificent specimens; it is there deposited from its solution in water acidulated by carbonic acid, and substances immersed in this water become incrusted by carbonate of lime when the excess of acid flies off. A fibrous carbonate of lime, called *satin-spar*, is found in Cumberland.

A peculiar variety of carbonate of lime, originally found in Arragon, in Spain, has been termed *Arragonite;* it often occurs in six-sided crystals of a reddish color, and is harder than the common carbonate. There is also an acicular or fibrous variety, found in France and Germany.

All the varieties of *marble* and *limestone* consist essentially of carbonate of lime; of these, *white granular limestone*, or *primitive marble*, is most esteemed; there are, also, many colored varieties of extreme beauty. The most celebrated statuary marble is that of Paros, and of Mons. Pentelicus, near Athens; and of Carrara, or Luni, on the eastern coast of the Gulf of Genoa; it is milk-white and less crystalline than the Parian. Many beautiful *secondary* marbles for ornamental purposes are quarried in Derbyshire, and especially the *black marble.* Westmoreland and Devonshire also afford varieties of ornamental marble; and in Anglesea, a marble intermixed with green serpentine is found, little inferior in beauty to the *verd antique.* Among the inferior limestones, we enumerate many varieties, such as *common marble; bituminous limestone*, abundant upon the Avon, near Bristol, and known under the name of *swine-stone*, or *stink-stone*, from the peculiar smell which it affords when rubbed; *Oolite*, or *Roestone*, of which the houses of Bath are built; *Portland-stone; Pisolite*, or *pea-stone*, consisting of small rounded masses composed of concentric layers, with a grain of sand in the centre; and lastly, *chalk* and *marl.*

All these substances are more or less employed for ornamental or useful purposes; they afford *quick-lime* when burned, and in that state are of great importance in agriculture, and as ingredients in the cements used for building.

SILICATES OF LIME.—There are several native silicates of lime; *apophyllite* is a hydrated potassio-silicate, and *datolite* and *botryolite* are hydrated boro-silicates of lime. Silicate of lime is also an ingredient in many varieties of glass, and in the slags of iron-furnaces. Silica and lime have been combined by fusion, but this requires a very high temperature, and the results have not been minutely examined; the most common silicate of lime is that in which the oxygen in the base is to that in the acid as 1 : 3 (CaO,SiO_3).

Mortars.—Lime and silica are the principal components of mortars and cements, but common mortar is a mixture rather than a compound. When lime, made into a paste with water, is applied to the surface of porous stones, or bricks, the greater part of the water is absorbed, and a layer of hydrated lime adheres to the surface: but this adhesion is much greater if the lime be previously mixed with two or three parts of silicious sand, and more especially if the too rapid absorption of the water be prevented by previously wetting the surface of the brick or stone to which the mixture is applied. Much of the excellence of the mortar depends upon the selection of the sand, which should be clean, sharp, and rather coarse-grained, and upon the quality of the lime, and the care with which they are blended; and it should be spread thinly, and not allowed to dry too rapidly. Under these circumstances it adheres firmly to the surfaces to which it is applied; and as it dries, it absorbs carbonic acid when exposed to the air, and a strong adhesion ensues between the lime and sand, in consequence, probably, of the formation of a thin layer of silicate of lime upon each grain of the latter. But although good mortar is excellent for all common purposes, it is soon disintegrated under water; and where buildings are to resist such action, peculiar kinds of limstones are required, so as to constitute what are called *hydraulic cements.* There are several substances more or less effective in imparting to mortar the valuable property of hardening under water. Limestone containing alumina, silicate of alumina, carbonate of magnesia, or oxide of iron, are of this class; and consequently, *meagre* limes as they are called, or limestones containing *clay*, afford, when burned, an hydraulic lime; and artificial mixtures of particular kinds of clay, with chalk or other limestones, and a proportion of sand, when duly calcined in properly constructed kilns, are employed for this important manufacture. *Portland cement*, and *Roman cement*, are hydraulic mortars or cements of this description; the former, when dry, resembling Portland stone; and the latter, being a substitute for the cements containing *puzzuolana*, a volcanic product found at Puzzuoli, near Naples, and long celebrated as conferring hydraulic properties on common lime: it contains the silicates of alumina, lime, and soda. The rapidity with which these cements harden in damp places, or when exposed to water, varies with their composition: 10 or 12 per cent. of clay confers hydraulic properties, but the cement requires about twenty days to harden. With 20 to 30 per cent. of clay, it sets in two or three days; and with 25 to 35 per cent. it is hard in a few hours. The last mixtures are those in common use for facing buildings, and when the cement is of good quality and very carefully prepared, it is extremely durable and weather-proof, and admits of elaborate moulding. A mixture of hydraulic mortar with coarse gravel, or broken flints, is largely used under the name of *concrete*, for the foundations of buildings; it soon hardens and becomes impermeable to moisture.

TESTS FOR LIME AND ITS SALTS.—A solution of *lime* (lime-water) is alkaline, and has the general properties of solutions of baryta and strontia, in reference to the action of nitrate of silver, and precipitation by carbonic acid, or any alkaline carbonate. It is distinguished from a solution of baryta, in not being precipitated by diluted sulphuric or fluosilicic acids; also by the fact that the precipitate given by oxalic acid in the solution, is not dissolved by an excess of the acid. In the last-mentioned character, lime resembles strontia; but the non-precipitation of lime by sulphuric acid furnishes a sufficient distinction. Of the three alkaline-earthy solutions, lime-water is the only one which yields a deposit when boiled.

The *soluble* salts of lime are neutral. They are precipitated—1. By alkaline carbonates and bicarbonates. 2. When the solutions are diluted, they are not precipitated by sulphuric acid or alkaline sulphates; 3. They are not precipitated by a solution of sulphate of lime, or chromate of potassa. 4. They are precipitated by oxalic acid, and oxalate of ammonia. The oxalate of lime is insoluble in oxalic and acetic acids, but is dissolved by mineral acids. The oxalate of ammonia will detect one part of lime in 50,000 of water; it is generally resorted to for the quantitative determination of lime. 73 parts of oxalate of lime carefully dried at 212°, indicate 28 of lime; or the oxalate may be converted, by a very low red heat, into carbonate of lime, or by a higher heat into quicklime. They are mostly soluble in nitric and hydrochloric acids. 5. When chloride of calcium is burnt in the flame of alcohol, it imparts to it an orange-red color. This is resolved by spectral analysis into green and orange bands (p. 58), no other alkaline metal giving a green color, excepting barium. Those salts of lime which are *insoluble* in water are nearly decomposed when boiled in solution of carbonate of soda or potassa, and so afford *carbonate of lime*.

MAGNESIUM ($Mg=12$).

Magnesium was first obtained by Davy in 1808, by passing the vapor of potassium over white-hot magnesia, but was not accurately examined till 1830, when Bussy prepared it by heating anhydrous chloride of magnesium with sodium. Bunsen and Matthiesen have recently procured this metal, by electrolyzing the fused chloride of magnesium. It is a silvery white, ductile, malleable metal; fusible at a red heat, volatile at the same temperature as zinc, and burns with great brilliancy, evolving an intensely white light when heated in the air. It is unchanged in dry air, and is only slowly oxidized in damp air. It does not decompose water and liberate hydrogen, but is rapidly dissolved by dilute acids. It burns when heated in chlorine, and in the vapor of bromine, iodine, and sulphur. It may be boiled in potassa without undergoing any change. Its sp. gr. is 1·74.

OXIDE OF MAGNESIUM. MAGNESIA (MgO).—This, which is the only compound of magnesium and oxygen, is procured by exposing carbonate of magnesia to a red heat. It forms a bulky white insipid powder, sp. gr. about 3·4, nearly insoluble in water, and having an alkaline reaction upon vegetable colors. Notwithstanding its great insolubility, the alkalinity of the oxide may be clearly proved by mixing a portion of it with blue infusion of cabbage or red litmus. The former is turned green, and the blue of the latter is restored. If the oxide is diffused in water, and a solution of sulphuretted hydrogen added, followed by a few drops of a solution of nitroprusside of sodium, a rich rose-pink color is brought out. Its basic character and power of displacing metallic oxides are also proved by mixing it with a solution of nitrate of silver; brown oxide of silver is separated. If arsenio-nitrate of silver is used, a yellow precipitate of arsenite of silver is produced. It is almost infusible, and a mixture of lime and magnesia is scarcely more fusible than the separate earths. It does not absorb carbonic acid, or moisture, when exposed to air, nearly so rapidly as the other alkaline earths; and scarcely any heat is produced by pouring water upon it, but it is converted into a *hydrate* (MgO,HO). When thrown down from its solutions by potassa, collected upon a filter, and dried at 212°, it still retains water; but at a temperature below redness, it becomes anhydrous. It is insoluble in solutions of potassa and soda. It forms bitter saline compounds with the acids; and is readily distinguished by the solubility and bitter taste of its sulphate. The attractions of magnesia for the acids correspond, in most instances, closely with those of ammonia, which is in some cases displaced by, and in others displaces, magnesia.

Native hydrate of magnesia exists in the serpentine rocks of Hoboken, in New Jersey; and in Unst, one of the Shetland Isles. It has a pale greenish hue, and a soft lamellar texture; sp. gr. 2·3. Sometimes it forms prismatic crystals.

NITRATE OF MAGNESIA (MgO,NO_5). This salt may be procured by digesting carbonate of magnesia in diluted nitric acid, and evaporating to produce crystallization. It is very deliquescent, and is obtained crystallized with difficulty, in rhomboidal prisms. It is soluble in half its weight of water, and in nine parts of alcohol. It has a cooling and bitter taste. It is decomposed at a red heat, leaving magnesia.

CHLORIDE OF MAGNESIA ($MgCl$) may be obtained by dissolving 1 part of magnesia in hydrochloric acid, and then adding 3 parts of sal-ammoniac, and evaporating the mixed solution to dryness. The resulting double salt ($NH_4,Cl,2MgCl$) is then decomposed by a red heat in a covered platinum crucible. When the sal-ammoniac is expelled, chloride of magnesium remains, and concretes on cooling; it forms a crystalline mass, which evolves heat when acted on by water. It cannot be obtained by simply evaporating its aqueous solution to dryness, for in that case hydrochloric acid escapes, and magnesia remains. When a concentrated solution of chloride of magnesium is exposed to a cold atmosphere, it yields prismatic hydrated crystals ($MgCl,6HO$), deliquescent, very soluble in water and alcohol, and of a bitter and biting taste. This salt is found in a few saline springs, and in the water of the ocean, forming a principal ingredient in the liquid which remains after the separation of sea salt, and which is usually called *bittern* (page 135). *Bromide of magnesium* is also a constituent of sea-water.

SULPHATE OF MAGNESIA (MgO,SO_3).—The commercial demands for sulphate of magnesia are chiefly supplied from sea-water, and from magnesian limestone. When sea-water is resorted to, the greater part of the common salt is first removed by evaporation, and the remaining *bittern*, consisting chiefly of a solution of chloride of magnesium and sulphate of magnesia, is boiled down with the addition of sulphuric acid, or with sulphate of soda, by either of which the chloride is ultimately decomposed and converted into sulphate. The bittern may be also decomposed by hydrate of lime, and the resulting precipitate afterwards treated by sulphuric acid, by which sulphate of magnesia and sulphate of lime are obtained. When magnesian limestone is used as a source of sulphate of magnesia, it is calcined, and reduced to powder by sprinkling it with water; it is then diffused through water, and sulphuric acid is added, and as sulphate of magnesia is so much more soluble than sulphate of lime, it is easily separated. A solution of sulphate of lime may be also decomposed by carbonate of magnesia, as is sometimes seen, where water holding sulphate of lime in solution, filters through strata of magnesian limestone. The sulphate of magnesia from bittern is sometimes preferred as a source of magnesia, or of carbonate of magnesia, in consequence of the absence of iron, traces of which are always discoverable in the sulphate obtained from magnesian limestone; but as the latter is free from chloride of magnesium, and consequently not deliquescent, and may be obtained nearly pure, it is generally preferred for medicinal use.

There are some saline springs, or mineral waters, in which sulphate of magnesia is the leading ingredient, as those of Seidlitz, Seydschutz, Egra, and formerly those of Epsom in Surrey, whence the name of *Epsom salt;* it is also largely obtained in some alum works. It not unfrequently occurs as a fine capillary incrustation upon the damp walls of cellars and new buildings. It has been found *native*, constituting the *hair salt* of mineralogists. It appears to be produced, in some springs, by a reaction of sulphate of lime in the water, on carbonate of magnesia in the soil.

Crystallized sulphate of magnesia ($MgO,SO_3,7HO$), forms, at ordinary temperatures, four-sided prisms with reversed dihedral summits; or four-sided pyramids. When the crystals are formed at about 70° to 80°, they contain 6HO: at 32° they are large and contain 12HO. Their density is 1·7. Exposed to air, the salt has, when pure, a slight tendency to efflorescence, but the salt of commerce is often deliquescent from the presence of chloride of magnesium. Its taste is saline and bitter. The crystals are soluble in about their own weight of water at 60°, and in three-fourths their weight of boiling water. When exposed to heat, they readily lose six equivalents of water, but retain one equivalent, up to 500. At a red heat this salt becomes anhydrous, and at a higher temperature it runs into a white enamel. The anhydrous salt regains water from the atmosphere, and when sprinkled with water evolves much heat.

The aqueous solution of sulphate of magnesia furnishes a precipitate of hydrated carbonate, upon the addition of carbonate of potassa, or of soda; but carbonate of ammonia does not even render it turbid, unless heat be applied, in which case a precipitate is also thrown down. The alkaline bicarbonates occasion no precipitate when added to a cold solution of sulphate of magnesia, but after some hours crystals of hydrated carbonate of magnesia are deposited.

Ammonio-sulphate of Magnesia ($NH_4O,MgO,2SO_3,6HO$) may be obtained by mixing solution of sulphate of ammonia with solution of sulphate of magnesia; if the solutions are concentrated, it falls as a white crystalline powder; or by pouring ammonia into a solution of the sulphate of magnesia, in which case, part only of the magnesia is thrown down, the remainder forming, with the sulphate of ammonia, this salt. It crystallizes in oblique rhombic prisms.

Sulphate of Potassa and Magnesia ($KO,MgO,2SO_3,6HO$) forms rhomboidal crystals, scarcely more soluble than sulphate of potassa, and of a bitter taste.

Sulphate of Soda and Magnesia ($NaO,MgO,2SO_3,6HO$) forms truncated rhombic crystals, soluble in about five parts of water at 60°.

PHOSPHATES OF MAGNESIA. *Tribasic phosphate of magnesia and water* ($2(MgO)HO,PO_5+14HO$).—This phosphate is formed by mixing a solution of two parts of crystallized sulphate of magnesia in 32 of water, with a solution of three parts of common crystallized phosphate of soda in 32 of water: after twenty-four hours, acicular crystals are deposited, having the above formula. They effloresce in the air, and are sparingly soluble in water, but readily soluble in dilute acids. At a red heat this salt becomes a *pyrophosphate*$=2(MgO)PO_5$.

PHOSPHATE OF AMMONIA AND MAGNESIA ($2(MgO)NH_4O,PO_5+12HO$).—This salt, formerly designated *triple phosphate*, is produced when ammonia, or an ammoniacal salt, is added to a mixture of common phosphate of soda with any magnesian salt. Thus on adding ammonia or carbonate of ammonia to a mixed solution of phosphate of soda, and sulphate of magnesia, the ammonia-magnesian phosphate falls in the form of a white granular precipitate, insoluble in the liquid from which it is thrown down, but sparingly soluble in pure water, so that it cannot be washed upon the filter without loss. It is readily soluble in the greater number of diluted acids. If bicarbonate of ammonia is used in its formation, it falls slowly, but its appearance is accelerated by drawing lines with a glass rod upon the surface of the glass or basin containing the mixed solutions, when the double phosphate presently appears upon those lines. When this phosphate is heated, it loses water and ammonia, and at a red heat, glows like tinder, and leaves a phosphate of magnesia$=2MgO,PO_5$, containing therefore 35·7 per cent. of magnesia. It is often resorted to for the determination or the presence, and of the quantity of magnesia.

This salt is frequently deposited from urine, in the form of white sand, or as a superficial crystalline film, especially in cases where the natural acidity of the urine is diminished by diet, medicine, or morbid action, constituting what has been termed the phosphatic diathesis; it frequently forms urinary calculi; and it occurs in intestinal concretions. The presence of phosphate of magnesia in the husk of grain, in the potato, and other plants, is important to the agriculturist, and shows why phosphoric acid and magnesia are contained in fertile soils: its existence in urine, and almost animal manures, contributes therefore to their efficacy: it has been said especially to promote the growth of potatoes. It may be detected, in considerable quantity, in good malt liquor.

CARBONATE OF MAGNESIA. *Magnesia alba.*—This term is applied to the precipitate obtained by adding carbonate of soda to a solution of sulphate of magnesia, and edulcorating and drying it: it is generally obtained from boiling solutions, and great attention should be paid to the purity of the water employed in washing the precipitate, and to the method of drying it, It usually contains from 40 to 43 per cent. of magnesia, 36 to 37 of carbonic acid, and from 20 to 22 of water; so that it may be regarded as $=5MgO$,

$4CO_2,6HO$: or 4 atoms of monohydrated carbonate, in combination with 1 atom of binhydrate of magnesia.

A light and a heavy carbonated magnesia are prepared for pharmaceutical use, dependent upon the strength of the solutions from which they are precipitated: if these be dilute, it is light and bulky; if more concentrated, the product is more dense.

Native Carbonate of Magnesia has been found in Piedmont and Moravia, and at Hoboken, in North America, in veins in a serpentine rock, accompanying the *native hydrate.* A variety of *native carbonate of magnesia* has also been brought from India.

When a current of carbonic acid is passed through a mixture of water and carbonate of magnesia, under pressure, a clear solution is obtained, which has a bitter taste, and which, when surcharged with carbonic acid, affords a useful medicinal preparation; but a crystallized *bicarbonate* of magnesia cannot be obtained.

Carbonate of Potassa and Magnesia ($KO,2MgO,4CO_2+9HO$).—When excess of bicarbonate of potassa is mixed with chloride of magnesium, no precipitation ensues, but in a few days crystals are formed, of an alkaline taste, which are decomposed by hot water.

Carbonate of Soda and Magnesia is formed as the double potassa salt, by bicarbonate of soda. When magnesia is precipitated by carbonate of soda, a portion of the double soda salt is retained, unless the liquid is boiled. An excess of sulphate of magnesia easily dissolves the precipitated carbonate.

Carbonate of Lime and Magnesia is the mineral known under the name of *bitter spar;* it has the primitive form of carbonate of lime, and consists of one atom of each of its component carbonates. *Dolomite,* or magnesian carbonate of lime, is similarly constituted, being MgO,CO_2+CaO,CO_2. Some varieties of bitter spar and dolomite are also $=3(CaO,CO_2)+2(MgO,CO_2)$, and $2(CaO,CO_3)+(MgO,CO_2)$. The formula of *Conite* is $CaO,CO_2+3(MgO,CO_2)$.

Some of the magnesian limestones are well adapted for rough sculpture, and building materials; but when porous, or granular, they are subject to decay, especially in a London atmosphere, where the rain always brings down some sulphate of ammonia, a salt which acts on the magnesian limestone, forming carbonate of ammonia, and sulphate of magnesia and lime: these sulphates, by crystallizing in the pores of the stone, tend to its gradual disintegration. It has been attempted to check this crumbling, by washing the surface first with a solution of silicate of soda, and then with chloride of calcium, so as to form an insoluble silicate of lime in the pores of the stone, which tends to cement and indurate it, and trials of this kind are now being made at the Palace of Westminster: how far it may be possible to arrest the decay unfortunately going on in many parts of that building remains to be proved.

Borates of Magnesia.—Several of these salts have been described, but the only one of interest is *Boracite.* It is to be found in Holstein. Its primitive form is a cube, but the edges and angles are generally replaced by secondary planes: these crystals become electric by heat, the most complex angles being rendered positive, and the simplest negative. It sometimes contains lime. Its sp. gr. is 2·95: it is difficultly fusible before the blowpipe, insoluble in water, and slowly soluble in acids. It consists of 3 atoms of magnesia combined with 4 of boracic acid.

Silicates of Magnesia.—These compounds are difficult of fusion, but become less so by the addition of silicate of lime: the neutral silicate, MgO,SiO_3, may be melted in a blast-furnace. *Native silicates of magnesia* are abundant: the varieties of *serpentine* are silicates combined with hydrates of magnesia. *Talc*, *steatite*, *soap-stone*, *French-chalk*, and *meerschaum*, are also magnesian silicates: and *Jade*, so extensively used for ornamental purposes by the Chinese, is a silicate of magnesia and lime. *Olivine*, or *chrysolite*, found in igneous rocks, and occasionally accompanying meteoric iron, is a silicate of magnesia and iron. Many other double magnesian silicates are common mineral products.

TESTS FOR MAGNESIA AND ITS SALTS.—The oxide of magnesium, or magnesia, is distinguished from the other alkalies and alkaline earths, by its insolubility in water. With this exception, it has the usual properties of an alkali in its action on vegetable colors, and on a solution of nitrate of silver. It is dissolved by acids, forming the *salts* of magnesia, which are neutral and characterized by a bitter taste.

The aqueous solutions are precipitated: 1. By potassa or soda, the precipitate being soluble in hydrochloric, nitric, and sulphuric acids, and in hydrochlorate, nitrate, and sulphate of ammonia, but not in potassa or soda. 2. Ammonia throws down only part of the magnesia from a diluted solution, and forms a double salt. The precipitated hydrate of magnesia is soluble in hydrochlorate of ammonia. Ammonia does not precipitate the solutions of any other alkali or alkaline earth. 3. Carbonate of potassa or soda throws down only a part of the magnesia, unless the solution is heated, when nearly the whole is precipitated. Sal-ammoniac redissolves this precipitate, and when previously added to the magnesian solution, no precipitate ensues on adding the alkaline carbonates, unless the liquor is heated. 4. The carbonate of ammonia and bicarbonates of potassa and soda give no precipitate in magnesian solutions, except the liquor be boiled. These tests distinguish a magnesian salt from the salts of baryta, strontia, and lime, which are precipitated in the cold. 5. Common phosphate of soda only precipitates *concentrated* magnesian solutions, but if ammonia or carbonate of ammonia be added, the magnesia is precipitated in the form of ammonio-magnesian phosphate, insoluble in hydrochlorate of ammonia, and diluted ammonia. Moistened with acetate of cobalt, and heated before the blowpipe, the magnesian salts give pale rose-colored compounds: the tint is only distinct on cooling, and never very intense. 6. Sulphuric acid and the alkaline sulphates, oxalic acid and the oxalates, give no precipitate in a solution of a salt of magnesia. 7. A magnesian salt, if pure, gives no color to the flame of alcohol.

In quantitative analysis, magnesia is almost always precipitated by a solution of phosphate of soda, to which ammonia or its carbonate has been previously added; it is collected and washed with the precautions above mentioned, and ignited so as to be weighed in the state of pyrophosphate. Every 100 parts of ammonio-magnesian phosphate, dried at 60°, indicate 16·26 of magnesia: every 100 parts of its residue, after ignition, indicate 35·7 parts of magnesia.

CHAPTER XXVII.

ALUMINUM—GLUCINUM—ZIRCONIUM—THORINUM—YTTRIUM—ERBIUM—TERBIUM—CERIUM—LANTHANUM—DIDYMIUM.

ALUMINUM ($Al=14$).

ALUMINUM is obtained by passing the vapor of chloride of aluminum over sodium, heated in a porcelain tube: intense ignition ensues, and the reduced aluminum forms metallic globules: ($Al_2Cl_3+3Na=2Al+3NaCl$). The mineral called *cryolite* (a double fluoride of aluminum and sodium) has also been used as a source of the metal, and is decomposed when heated with sodium, yielding globules of aluminum, imbedded in fused fluoride of sodium. The changes which take place may be thus represented: $Al_2F_3,3NaF+3Na=2Al+6NaF$.

Aluminum is a white malleable and ductile metal, of about the hardness of silver; its specific gravity, when rolled, is about 2·67, and when cast 2·56. Its point of fusion is, according to Deville, 1750°. It is not acted upon by air or water at common temperatures, but damp air slowly tarnishes it. When intensely heated in a current of air, it suffers only slight oxidation: heated to redness in an atmosphere of steam, it is slowly oxidized. It is readily acted upon by hydrochloric acid, which evolves hydrogen and forms chloride of aluminum: neither sulphuric nor nitric acid affects it at common temperatures, but when boiled in the latter, it is oxidized so long as the heat is maintained. In concentrated solutions of potassa and soda it is oxidized, and hydrogen is liberated. This action is increased when the alkaline solution is heated. It forms alloys with many of the other metals, but does not combine with mercury. It is not affected by sulphur or sulphuretted hydrogen. The general characters of this metal are such as to fit it for many useful purposes, but its high price has hitherto limited these applications.

OXIDE OF ALUMINUM. ALUMINA (Al_2O_3).—To obtain *alumina* we decompose a solution of *alum* by excess of carbonate of potassa, wash the precipitate with repeated portions of hot distilled water, redissolve it in hydrochloric acid, precipitate it again by ammonia, and thoroughly edulcorate, and dry the precipitate: it is rendered anhydrous by exposure to a red heat. In this process, the alumina which first falls always retains a little alkali, which is got rid of by the second solution, and precipitation by ammonia; if ammonia be used as the original precipitant of a solution of alum, the resulting precipitate retains subsulphate of alumina, not decomposable by excess of ammonia. Pure alumina may also be obtained by igniting pure *ammonia-alum*, sulphate of ammonia evaporates, and alumina remains, perfectly white, and soft to the touch, but almost insoluble in acids.

Alumina is a colorless, insipid, and insoluble powder, without action upon vegetable blues. It does not set free oxide of silver from a solution of nitrate; and when diffused in water, it produces no change of color with sulphuretted hydrogen and a solution of nitro-prusside of sodium. Its specific gravity is 2; but after exposure to an intense heat, about 4. By the oxyhydrogen blowpipe it may be fused into a colorless globule. It has a strong attraction for moisture, which it rapidly absorbs from humid air, to the amount of one-third of its weight. When mixed with water, alumina is characterized by the plasticity of the mixture; and if the paste be dried in the air, and then heated, it shrinks considerably in consequence of the loss of water. Alumina has a strong affinity for various organic compounds, and its use in the arts of dyeing and calico-printing depends upon its attraction for different coloring-principles, and for ligneous fibre. If ammonia be added to a solution of alum in infusion of cochineal, or of madder, the alumina falls in combination with the coloring-matter, and the supernatant liquor remains colorless. Colors thus prepared are called *Lakes.*

Moist alumina is readily soluble in most of the concentrated acids; but after the expulsion of its water by heat, it is more difficultly dissolved, or even insoluble. It is sparingly soluble (when moist) in caustic ammonia; but potassa and soda readily dissolve it; it is also soluble, to a small extent, in the aqueous solutions of baryta and strontia. The fixed alkaline solutions of alumina are decomposed by the acids, and by ammoniacal salts.

Alumina, like other sesquioxides, is a comparatively feeble base; none of its salts are, in fact, neutral, but have an acid reaction; and in respect to the more powerful basic oxides, it has been represented as performing the part of an acid, so that such compounds have been termed *Aluminates.* Many of these combinations exist native.

Alumina is recognized by its solubility in caustic potassa; by the formation of octahedral crystals of alum on evaporating its sulphuric solution with the addition of sulphate of potassa; by the astringent sweetness of this sulphate; and by the blue color which it affords when moistened with nitrate of cobalt and strongly heated.

Native alumina may be said to constitute the *sapphire,* which occurs either colorless or pale-blue, is extremely hard, and occasionally crystallized; its specific gravity is about 3·5. The oriental *ruby* and the oriental *topaz* are red and yellow varieties of sapphire. *Corundum, adamantine spar,* and *emery,* also consist chiefly of alumina, with less than 2 per cent. of oxide of iron, and a trace of silica: the specific gravity of corundum is about 4. All these substances are extremely hard, being, in that respect, second only to diamond.

HYDRATES OF ALUMINA.—Alumina, precipitated from its solutions, and dried at between 70° and 80°, retains about 60 per cent. of water; but its physical characters vary, dependent upon the strength of the solution from which it is precipitated. When thrown down from a saturated solution of alum, it is pulverulent; but from a dilute solution, gelatinous: the pulverulent hydrate loses its water at a red heat. *Diaspore* and *Gibbsite* are *native* hydrates of alumina.

CHLORIDE OF ALUMINUM (Al_2Cl_3).—This compound is obtained as follows: Alumina is mixed into a paste with powdered charcoal, oil, and sugar, and this is heated in a covered crucible till the organic matter is decomposed: an intimate mixture of the alumina with charcoal is thus obtained, which is introduced, whilst hot, into a porcelain tube, placed in a convenient furnace; dried chlorine is then passed through it into a receiver attached to the other end of the tube, and the air being thus expelled, the tube is heated red-hot, and chlorine gradually passed into it; carbonic oxide is disengaged, and chloride of aluminum formed, which chiefly collects within the tube, and ultimately plugs it up. It is a crystalline translucent substance, of the color of chlorine; it fumes and deliquesces when exposed to air; it is energetically acted upon by water, and is very soluble in alcohol; it may be preserved in naphtha. When a solution of alumina in hydrochloric acid is evaporated, a deliquescent hydrated chloride remains, which at a higher temperature evolves hydrochloric acid and leaves alumina.

SULPHATE OF ALUMINA ($Al_2O_3,3SO_3$) is formed by digesting hydrate of alumina in sulphuric acid diluted with an equal bulk of water; the solution is evaporated and alcohol added, which throws down the tersulphate. It dissolves in 2 parts of water, and forms small lamellar crystals, of a sweet and astringent taste, which include 18 atoms of water. When excess of hydrated alumina is boiled in the diluted acid, and the solution filtered, and evaporated *in vacuo* over sulphuric acid, it congeals into a soft, white, semitransparent mass, which may be dried on blotting paper, and is not altered by the air.

BASIC SULPHATE OF ALUMINA ($Al_2O_3,SO_3,9HO$).—When ammonia is added to a solution of sulphate of alumina, a white powder falls, which is not decomposed by excess of ammonia, and which, when well washed and carefully dried, has the above formula. It exists native, forming the mineral called *aluminite*.

SULPHATE OF ALUMINA AND POTASSA; COMMON ALUM; POTASSA-ALUM (KO,SO_3; $Al_2O_3,3SO_3$; $24HO$).—This useful salt is manufactured upon an extensive scale. *Aluminous slate*, or *shale*, which is an argillaceous slaty rock containing sulphide of iron, is roasted so as to oxidize the iron and acidify the sulphur; on lixiviating the roasted ore, a *sulphate of alumina* is obtained, which, with the addition of *sulphate of potassa*, yields alum. The *shales* or wastes of old coal mines, which fall down in a decomposing state, yield, on lixiviation, especially after prolonged exposure to air and moisture, considerable quantities of sulphate of alumina and sulphate of iron; the solution of these salts is evaporated, and, when sufficiently concentrated, is run out into coolers, where the sulphate of iron crystallizes, and the sulphate of alumina, being more soluble, remains in the mother-liquors. To these, when heated, sulphate, or chloride of potassium is added, and they then yield crystals of alum, not at first pure, but rendered so, and obtained in beautifully-perfect octahedra, by recrystallization. When chloride of potassium is used, it decomposes the sulphate of iron of the alum-liquors, forming chloride of iron and sulphate of potassa; the latter salt goes to the formation of alum, leaving the chloride of iron in solution. There are other methods of manufacturing alum, such as by the decomposition of clay by sulphuric acid, and by the lixiviation of certain *alum stones*, as they are called, which are products of the joint action of sulphurous acid and oxygen upon volcanic rocks containing alumina and potassa.

Ordinary alum has a sweet and astringent taste, accompanied by some degree of acidity; its sp. gr. is 1·72: it reddens vegetable blues: it dissolves in about 16 parts of cold water, and in less than its weight of boiling water. The crystals are permanent in the air, or only very slightly efflorescent in a dry atmosphere; when heated, they fuse in their water of crystallization, and when this is expelled the dry alum becomes opaque and spongy, and in this state is termed *roche alum*, or *burnt alum*. At a temperature of 140°, alum gradually loses 18 atoms of its water of crystallization. When long retained in fusion it loses 18·95 per cent. of water, and ultimately forms a vitreous mass, which retains 14 atoms of water: if in this state it be kept at a temperature of 248° for 12 hours, the loss of water amounts to about 38 per cent. and it forms a porous mass retaining 5 atoms of water; it then remains unchanged up to 320°; but at 356 it sustains a farther loss of water, amounting on the whole to 43·5 per cent., so that the residue only retains one atom of water, which is not expelled under a temperature approaching to redness. Anhydrous alum gradually absorbs water from the atmosphere. When freshly prepared, and put into water, it appears almost insoluble, and remains for a long time nearly unchanged; but if previously exposed to the atmosphere, it dissolves more readily. At a red-heat, alum first loses that portion of its acid belonging to the alumina, and ultimately the sulphate of potassa is itself decomposed under the influence of the alumina, which combines with the potassa and displaces the sulphuric acid.

CUBIC ALUM.—If the quantity of carbonate of soda necessary to neutralize a portion of alum, be divided into three equal portions, and added in a gradual manner to the aluminous solution, it will be found that the alumina first precipitated is redissolved upon stirring, and that no permanent precipitate is produced till nearly 2 parts of alkaline carbonate are added. It is in the condition of this partially-neutralized solution that alum is generally applied as a mordant. When this solution is concentrated, alum crystallizes from it, generally in the cubic form, and the excess of alumina is precipitated.

Alum is a salt of extensive use in the arts, especially for the preparation of mordants employed by the dyer and calico-printer; it is also employed in preparing and preserving skins; in pharmacy it is used as an astringent and a styptic.

Potassa is not easily discovered in potassa-alum until the alumina has been removed. Thus neither fluosilicic acid nor tartaric acid will precipitate potassa from a concentrated solution; and chloride of platinum produces after a time only a slight turbidness. Potassa-alum may, however, be easily identified by the lilac color given to flame when a small portion of the powder is heated beyond fusion on fine platinum wire; soda-alum gives under the same circumstances a yellow color; and ammonia-alum, if free from these two bases, imparts no color to flame.

Homberg's Pyrophorus.—When potassa-alum is ignited with charcoal, a spontaneously-inflammable compound results, which has long been known under the name of *Homberg's pyrophorus.* The potassa is decomposed in this process, as well as the acid of the alum; the pyrophorus is probably a compound of sulphur, charcoal, potassium, and aluminum.

SULPHATE OF ALUMINA AND AMMONIA. AMMONIA-ALUM (NH_4O,SO_3; $Al_2O_3,3SO_3$; $24HO$).—This salt is obtained exactly as the preceding, only *sulphate of ammonia* is substituted for sulphate of potassa: its atomic constitution also resembles that of potassa-alum; and it is so similar in other respects, that, as far as mere appearance and more obvious properties are concerned, the two salts are not readily distinguished. It is recognized by evolving ammonia, when triturated with lime or potassa. This variety of alum is manufactured on a large scale with the sulphate of ammonia derived from gas-works. When heated it loses water, then ammonia, and at a very high heat, its acid, the residue being pure alumina.

SULPHATE OF ALUMINA AND SODA. SODA-ALUM (NaO,SO_3; $Al_2O_3,3SO_3$; $24HO$). This salt is formed when the sulphate of potassa of common alum is replaced by sulphate of soda; it crystallizes in octahedra, which are less hard, smooth, and regular, than those of potassa-alum; they effloresce in dry air, and at 110° to 120° become opaque and gradually lose their water of crystallization, the whole of which is expelled at a red heat. They dissolve in 2·14 of water at 55°, and in their own weight at 212°.

The three alums are isomorphous, and the bases may replace each other without altering the crystalline form. So the alumina may be replaced by isomorphous oxides—*e. g.* the sesquioxides of iron, chromium, and manganese; hence the following may be taken as a general formula for the alums: $KO(NH_4O,NaO,CæO,RbO)SO_3,Al_2O_3(Fe_2O_3,Cr_2O_3Mn_2O_3)3SO_3,24HO$. (p. 37).

Sulphate of Alumina and Lithia. Lithia-Alum ($LiO,SO_3;Al_2O_3,3SO_3;24HO$).—When an aqueous solution of sulphate of lithia and sulphate of alumina is subjected to spontaneous evaporation at a temperature not exceeding 52°, it yields octahedral and rhombic dodecahedral crystals soluble in 24 parts of cold, and 0·87 of boiling water.

The new alkalies, *cæsia* and *rubidia* also form alums with sulphate of alumina, similar in constitution and form to potassa-alum.

Phosphates of Alumina.—Common phosphate of soda gives a gelatinous precipitate with solution of alum, which drives into a white insipid powder, insoluble in water, and in solution of sal-ammoniac, but soluble in acids and in solution of potassa. The mineral known under the name of *Wavellite* is a *hydrated phosphate of Alumina*, $3Al_2O_3; 2PO_5,12HO$. *Turquois* or *Calaite* is a phosphate of alumina$=2(Al_2O_3)PO_5+5HO$, colored by oxide of copper. *Ambligonite* is a phosphate of alumina and lithia, and *Lazulite* contains phosphate of alumina with phosphate of iron.

Alumina does not combine with carbonic acid.

Silicates of Alumina.—All the varieties of *clay* are silicates or hydrated silicates of alumina; they are frequently largely mixed with other substances, but their important uses in agriculture and the arts are referable to the above silicate. Several minerals are definite crystalline silicates, which by disintegration or decomposition, contribute to the formation of clay; common felspar is a silicate of alumina and potassa; $Al_2O_3; 3SiO_3+KO,SiO_3$: it is one of the constituents of *granite*, and some of its varieties crumble, when exposed to the joint action of air and water, into a white clay: *Cornish clay*, and the *Kaolin* of China, are clays so formed, and may be represented as $Al_2,O_3; 3SiO_3+2HO$. Other clays are less pure, from the admixture of sand, oxide of iron, or carbonate of lime, substances which importantly modify their properties. The varieties of *marl* are calcareous clays; and the *colored clays* generally derive their various tints from the oxides of iron. The presence of these and some other extraneous matters, renders some clays very fusible: the pure aluminous silicates are nearly infusible, but when lime, magnesia, or oxide of iron, is present, they become more or less fusible or vitrifiable, in proportion to the quantity of these bases present in the clay. The varieties of *fire-clay* used for lining furnaces, and other similar purposes, are nearly pure silicates$=Al_2,O_3,3SiO_3$, with mere traces of alkaline bases and oxide of iron. The different red and yellow *ochres*, and *boles*, are mixtures of clay and hydrated peroxide of iron; some of them contain oxide of manganese. *Fuller's earth*, used for the capillary absorption of greasy matters, is also a porous silicate of alumina. Clay has some remarkable distinctive properties; it exhales a peculiar odor when wetted or breathed upon, and when dry and applied to the tongue, it adheres to it, in consequence of the rapidity with which it absorbs moisture; it readily absorbs ammonia, and many other gases and vapors generated in fertile and manured soils; hence its agricultural value. The important quality of *plasticity*, upon which the manufacture of porcelain and pottery depends, belongs exclusively to aluminous combinations in their humid state, so that they admit of being turned in the lathe or upon the potter's wheel, or of being moulded into the infinite variety of useful and ornamental products of the ceramic art. These forms are rendered permanent by careful drying, and subsequent exposure to high temperatures.

Tests for the Salts of Alumina.—These salts have an astringent, sweet, and subacid taste, and redden litmus. 1. They are precipitated by potassa or soda, but the precipitate is redissolved when the alkalies are added in excess, but are again precipitated by hydrochlorate of ammonia. 2. The precipitate produced by ammonia is not soluble to any extent in excess of that alkali, and it is not dissolved by hydrochlorate of ammonia. 3. The carbonates and bicarbonates of potassa, soda, and ammonia, throw down hydrated alumina, with the escape of carbonic acid, and the precipitate is nearly insoluble in an excess of the precipitants. 4. Sulphate of potassa, with a little sulphuric acid, added to an acid solution of alumina, deposits, by concentration, a crystalline compound, which is *alum.* 5. Phosphate of soda produces a flocculent precipitate of phosphate of alumina. 6. When aluminous substances are heated by the blowpipe with nitrate of cobalt, they acquire a blue color, which is only distinctly seen by daylight after the mixture has cooled. 7. Hydrosulphate of ammonia gives a precipitate which is gelatinous hydrate of alumina—sulphuretted hydrogen being set free. This result is owing to the action of ammonia—as sulphuretted hydrogen produces no precipitate (of sulphide) in the solutions. The gelatinous hydrate is readily dissolved by a solution of potassa. This test serves to distinguish a solution of alum from one of magnesia, since unless the hydrosulphate contain free ammonia, it will give no precipitate with a salt of magnesia. If a precipitate is formed (by reason of the presence of ammonia) it is recognized as hydrate of magnesia by its being dissolved by hydrochlorate o ammonia. Hydrate of alumina is insoluble in this liquid. Ferrocyanide of potassium has no action upon a salt of alumina.

Pottery and Porcelain.—The better kind of *pottery*, called in this country *Staffordshire ware*, is made of a mixture of alumina and silica; the former obtained in the form of a fine clay, from Devonshire chiefly, and the latter, consisting of chert or flint, heated red-hot, quenched in water, and then reduced to powder. Each material, carefully powdered and sifted, is diffused through water, mixed by measure, and brought to a due consistency by evaporation: it is then highly plastic, and may be formed upon the potter's wheel and lathe in circular vessels, or moulded into other forms, which, after having been dried in a warm room, are inclosed in baked clay cases, called *seggars;* these are ranged in a kiln so as nearly to fill it, leaving only space enough for the fuel; here the ware is kept red hot for a considerable time, and thus brought to the state of *biscuit.* This is afterwards *glazed*, which is done by dipping the biscuit-ware into a tub containing a mixture of about 60 parts of litharge, 10 of clay, and 20 of ground flint, diffused in water to a creamy consistence, so that when taken out, enough adheres to the piece to give an uniform glazing when again heated. The pieces are then again packed up in the seggars, with small bits of pottery interposed between each, and fired in a kiln as before. The glazing-mixture fuses at a moderate heat, and gives an uniform glossy coating, which finishes the process when it is intended for common white ware. The presence of lead in glazes is often objectionable, and may be dispensed with by using borax, which, however, is too expensive for common use. 100 parts of silica, 80 pearlash, 10 nitre, and 20 lime, fused, and then finely powdered, form a good glaze.

Glazed cast-iron vessels for culinary and other purposes are manufactured, in which the absence of lead in the glaze is important: those manufactured at Wolverhampton are glazed with a mixture of borax, potter's clay, and pulverized flints, to which powdered plate, or crown glass (free from lead), and a little carbonate of soda, are added. These ingredients are fused together; and the mass, reduced to a fine powder, is mixed with water and applied to the clean surface of the iron, upon which it is dried, and vitrified by exposure to heat in a muffle.

The patterns upon ordinary earthenware, which are chiefly in blue, in consequence of the facility of applying cobalt, are generally first printed off upon paper, which is applied to the plate, or other article, while in the state of biscuit; the color adheres permanently to the surface when heat is properly applied. In the manufacture of *porcelain*, the materials are so selected that the compound shall remain perfectly white after exposure to heat, endure a high temperature without fusing, and at the same time acquire a semivitreous texture, and a peculiar translucency and toughness. These qualities are united in some of the Oriental porcelain, or *China*, and of the French, English, and German porcelain. The Berlin porcelain, so justly esteemed in the laboratory, consists of about 71 silica, 24 alumina, 2 potassa, 1·5 protoxide of iron, and 1·5 lime and magnesia. The colors employed in painting porcelain, are the metallic oxides which are used for coloring glass; and in all the more delicate patterns they are laid on with a camel-hair pencil, and generally previously mixed with a little oil of spike-lavender or of turpentine. When several colors are used, they often require various temperatures for their perfection; in which case those that bear the highest heat are first applied, and subsequently those which are brought out at lower temperatures. This art of painting on porcelain, or in enamel, is of the most delicate description: much experience and skill are required in it, and with every care there are frequent failures. The gilding of porcelain is generally performed by applying finely-divided gold mixed up with gum-water and borax; upon the application of heat the gum burns off, and the borax vitrifying upon the surface, causes the gold firmly to adhere; it is afterwards burnished.

Crucibles composed of one part of good clay mixed with three of coarse sand, slowly dried and annealed, resist a very high temperature without fusion, and generally retain metallic substances; but when the metals oxidize, there are few which do not act upon earthen vessels; and when saline fluxes are used, the best of them suffer. Whenever silica and alumina are blended, the compound softens, and the vessel loses its shape if exposed to a white heat; this is even the case with *Hessian* crucibles. The most refractory of all vessels are those made entirely of clay, coarsely-powdered burned clay being used as a substitute for sand: these resist saline fluxes longer than others, and are therefore used for the pots in glass-furnaces. Plumbago is a good material for crucibles, and applicable to many purposes; when mixed with clay, it forms a very difficultly fusible compound, and is protected from the action of the air at high temperatures.

Lutes.—Under this term, a variety of compounds are used for securing the junctures of vessels, or protecting them from the action of heat. Slips of wetted bladder; linseed meal made into a paste with gum-water; white of egg and quicklime; glazier's putty, which consists of chalk and linseed oil; and *fat lute*, composed of pipeclay and drying-oil, are useful for retaining vapors; but to withstand the action of a high temperature earthy compounds are required. Loam, or a mixture of clay and sand well beaten into a paste and then thinned with water, and applied by a brush in successive layers, to retorts, tubes, &c., enables them to bear a high temperature; if a thick coating is required, care should be taken that the cracks are filled up as the lute dries; a little tow mixed with it renders it more permanent. If the lute is intended to vitrify, as, for instance, to prevent the porosity of earthenware at high temperatures, a portion of borax, or of red-lead, may be mixed with it.

GLUCINUM (G=7).

Glucinum is obtained by decomposing its chloride by means of sodium. It is a gray malleable metal, sp. gr. 2·1. Its fusing point is a little below that of silver: it is not altered by exposure to air, and is difficult of oxidizement, even in the flame of the blowpipe.

OXIDE OF GLUCINUM, or GLUCINA (G_2O_3), was first discovered in the *beryl:* it also exists in the *emerald*, in *euclase*, in the *chrysoberyl*, in *phenakite*, and in a few other rare minerals. It is white, insipid, and insoluble in water; it has no action on vegetable colors; its specific gravity is 2·97. It dissolves, especially in the state of hydrate, in solution of caustic potassa and soda, but not in ammonia. It differs from alumina in being soluble, when freshly precipitated, in carbonate of ammonia. With the acids it forms saline compounds of a sweetish astringent taste. From these solutions the carbonates of potassa and soda throw it down in the form of a bulky hydrated carbonate.

Characters of the Salts of Glucina.—These salts are astringent and sweet; they are precipitated by the caustic fixed alkalies, and the precipitate is redissolved by their excess, and sparingly by their carbonates: it is not soluble in caustic ammonia, but readily so in carbonate of ammonia, and the oxide is again precipitated on boiling the liquid. A characteristic property of glucina is, that when a warm solution of it is mixed with a warm solution of fluoride of potassium, till a precipitate begins to appear, and the mixture is then suffered to cool, a difficultly soluble double salt separates in the form of lamellar crystals. Sulphate of glucina does not form a crystallizable double salt (like alum) when mixed with sulphate of potassa.

ZIRCONIUM (Zr=34).

Zirconium is obtained by acting upon the potassio-fluoride of zirconium by potassium at a red heat. When cold the product is thrown into water, and the zirconium separates in the form of a black powder, having the appearance of plumbago. It is difficultly soluble in the acids, with the exception of the hydrofluoric, which readily dissolves it, evolving hydrogen. Heated in the atmosphere, it burns into zirconia.

OXIDE OF ZIRCONIUM; ZIRCONIA (Zr_2O_3) is of rare occurrence, having only been found in the *Zircon* or *Jargon*, and a few other scarce minerals. Zircon, when colorless and transparent, ranks among the gems: when colored brown or red, it is termed *hyacinth*. This mineral contains between 60 and 70 per cent. of zirconia, combined with silica and a little oxide of iron.

Zirconia is obtained by fusing finely powdered zircon with soda, saturating the product with hydrochloric acid, evaporating the solution to dryness, redissolving in water, and precipitating by excess of ammonia: the precipitate is then washed, dried, and ignited.

Zirconia is a white infusible substance, insoluble in water; specific gravity 4·3: it gives intense luminosity to the blowpipe flame. After having been heated to redness it resists the action of the acids, with the exception of the sulphuric. It is insoluble in caustic alkalies. *Chloride of Zirconium* forms efflorescent acicular crystals, soluble in water and in alcohol.

The Salts of Zirconia have an astringent taste. They are precipitated by caustic potassa, and the precipitate is not soluble in excess of the alkali. When boiled with sulphate of potassa, a sparingly soluble subsulphate of zirconia subsides. Infusion of galls produces in them a yellow precipitate; and phosphate of soda throws down a white phosphate of zirconia. The recently precipitated carbonate of zirconia is soluble in excess of bicarbonate of ammonia, or of potassa.

THORINUM, OR THORIUM (Th=60).

By passing a current of dry chlorine over a mixture of thorina and charcoal-powder, a crystalline *chloride of thorinum* is obtained, which is easily decomposed by potassium, and the product is *thorinum.* It is of a gray color, metallic lustre, and apparently malleable. It is not oxidized by water, but when heated in the air it burns into thorina. It is feebly acted on by sulphuric acid, and scarcely by nitric acid; it is not attacked by the caustic alkalies at a boiling heat. Hydrochloric acid dissolves it, with the evolution of hydrogen.

OXIDE OF THORINUM: THORINA (ThO).—This oxide, hitherto only found in a rare Norwegian mineral, *Thorite,* is white, and insoluble in the acids, with the exception of the sulphuric. When thrown down in the state of *hydrate* it dissolves more readily, and exposed to the air absorbs carbonic acid.

Thorina is distinguished from the other oxides by the following properties: from alumina and glucina, by its insolubility in pure potassa; from yttria, by forming with sulphate of potassa a double salt, which is insoluble in a cold saturated solution of sulphate of potassa; from zirconia, by the circumstance that after being precipitated from a hot solution of sulphate of potassa, it is almost insoluble in water and the acids. Thorina is precipitated also by ferrocyanide of potassium, which does not separate zirconia from its solutions. Sulphate of thorina is more soluble in cold than in hot water, so that a cold saturated solution becomes turbid when heated, and on cooling, recovers its transparency.

YTTRIUM (Y=32).

Yttrium is obtained by decomposing its chloride by potassium: it is gray, brittle, and resists the action of air and water.

Oxide of Yttrium, or Yttria (YO), was first discovered in *Gadolinite,* a mineral found at Ytterby, in Sweden; it also occurs in a very few other rare minerals.

ERBIUM. TERBIUM.

According to Mosander, Yttria is always accompanied by *Erbia* and *Terbia,* the oxides of two distinct metallic bases. Erbia is pale yellow, and Terbia pale red; but none of these substances have been adequately examined or identified.

CERIUM (Ce=46).

By heating chloride of cerium with potassium, an alloy is obtained which evolves hydrogen when put into water, and leaves cerium in the form of a gray metallic powder. Heated in the air it burns into an oxide, and it is soluble in the weakest acids with the evolution of hydrogen.

Cerium forms two oxides: the protoxide (CeO), which forms colorless salts; and the sesquioxide (Ce_2O_3), which forms red salts. Cerium has hitherto been found in a few minerals only, and it seems doubtful how far the properties ascribed to its oxides and salts, are not more or less dependent upon the presence of other bodies. Its most characteristic salt is the double sulphate of cerium and potassa. The oxalate of cerium has been lately employed in medicine.

LANTHANUM (La=44).

This metal is associated with Cerium. All its salts are said to be colorless. When the oxalate is heated, it leaves a white carbonate, which at a higher temperature, is converted into a light brown anhydrous oxide: the white hydrated oxide attracts carbonic acid so rapidly, that it cannot be completely washed upon a filter without conversion into carbonate.

DIDYMIUM (Di=48).

Didymium accompanies lanthanum and cerium in the minerals containing the latter metal. It appears to form one oxide only, of a brown color; and all its salts are colored, some being pink, others violet. The sulphate and nitrate are rose-colored; the hydrated oxide, carbonate, and oxalate are violet, and when ignited leave a dark-brown anhydrous oxide, readily soluble in dilute acids, and absorbing carbonic acid from the air.

The atomic weights attached to these metals are of doubtful accuracy. (Watts's *Jour. Chem. Soc.* ii. 131.)

CHAPTER XXVIII.

QUALITATIVE ANALYSIS OF THE OXIDES AND SALTS OF THE PRECEDING METALS.

THE oxides of the metals described in the preceding chapters form three well-marked groups. 1. The *Alkalies*, comprising potassa, soda, lithia, cæsia, and rubidia, to which may be added ammonia, the chemical characters of which have been considered on page 167. 2. *Alkaline earths*, baryta, strontia, lime, and magnesia; and 3. The *Earths*, of which only one is selected as a type of the others, namely, alumina.

The bases comprised in these three groups, whether in acid or neutral solutions, are not precipitated by a current of sulphuretted gas. One of them, alumina, is precipitated from its solution as hydrated oxide by a solution of sulphide of ammonium.

1. The *Alkalies.*—This name is applied to the oxides of those metals which are soluble in water and alcohol; they are marked by the following characters: 1. They have an acrid caustic taste. 2. They are corrosive to organic matter. 3. They neutralize acids, and form salts. 4. They combine with the oily acids to form soaps. 5. They exert a peculiar action on vegetable colors. As it is by the last-mentioned character that their presence is commonly recognized in analysis, it may be stated that an alkali restores the blue color to red litmus; that it renders blue infusion of cabbage green, and yellow tincture of turmeric red-brown. Blue litmus-paper reddened by a weak acid, turmeric-paper, or rose-paper (paper impregnated with a strong infusion of red roses), may be employed in the preliminary testing for alkalies. Well made rose-paper is nearly colorless, and it acquires a bright green color as the result of the action of a diluted alkali. If the alkaline solution is concentrated, the coloring matter is destroyed, and the rose-paper acquires a brownish-yellow tint. Blue infusion of cabbage, the method of preparing which has been elsewhere described (p. 70), is admirably adapted for a test-liquid. It acquires a red color from an acid solution, a green color from an alkaline solution, and it remains blue if the solution is neutral. The nitro-prusside of sodium is also a delicate test of alkalinity in a liquid. In order to employ it, a small quantity of sulphuretted hydrogen is passed into the suspected solution, and a few drops of nitro-prusside of sodium are added. A magnificent rose, purple, blue, or crimson color speedily manifests itself, according to the strength of the alkaline solution. The color soon disappears. This test thus indicates alkalinity in weak solutions of the phosphates, borates, carbonates, and even among the least soluble oxides, such as lime and magnesia (p. 335).

2. The *Alkaline Earths.*—These oxides have the general properties of alkalies, but they are specially marked by the following characters: 1. They are insoluble in alcohol, and much less soluble in water than the alkalies: one of them (magnesia) is nearly insoluble in water. 2. They form insoluble compounds with carbonic and phosphoric acids.

3. The *Earths.*—These oxides differ from the two preceding groups, in the following points: ,They are white tasteless powders. 2. They have no alkaline reaction. 3. They are insoluble in water and alcohol. 4. As hydrates, they combine with acids and alkalies to forms salts; and 5. Their oxides are not reducible at a red heat by hydrogen or carbon.

ACIDS, as contrasted with alkalies, have the property of rendering vegetable blues (litmus and cabbage) red. They neutralize alkalies and form salts. They exist in the gaseous, liquid, and solid state, sometimes soluble in water, at other times only sparingly so, as the boracic and arsenious acids; and in some instances quite insoluble, as calcined silicic acid. Those which are soluble are characterized by a sour taste, and sometimes by a strongly corrosive action on organic matter. Those only which are dissolved by water redden blue litmus-paper; this is the indication of acidity on which a chemist chiefly relies. The tests for the principal *acids* have been already described in the first part of the work.

Under each of the metals in the preceding chapters, the tests for its saline combinations have been given in detail. It will now therefore only be necessary to select a few of the more important of these tests, in order to show how the presence of a base belonging to one of the three groups of oxides, may be determined.

In this summary, we include among the *alkalies*, ammonia. Although not an oxide (page 168), it bears in its chemical properties the strongest analogies to potassa and soda, which are oxides of metals. Among the *earthy* bases, we select alumina as the only one which will probably present itself in the ordinary course of analysis.

The bases selected will be therefore the following: potassa (KO), soda (NaO), ammonia (NH_3), lithia (LiO), baryta (BaO), strontia (SrO), lime (CaO), magnesia (MgO), and alumina (Al_2O_3). It will be necessary to consider them (1) in the *uncombined* or free state, as bases; and (2) in the *combined* or saline state, as salts. The elements, radicals, and acids with which the metals or their oxides are supposed to be combined, have been already described in the chapters on the METALLOIDS; and to these the reader is referred for a description of the characters of each class of salts, in so far as they depend on the acid.

BASES.—Out of the nine bases selected, three may be at once recognized: *ammonia* by its odor and volatile reaction; and *magnesia* and *alumina* by their insolubility in water. The two latter may be dissolved in hydrochloric or sulphuric acid with certain precautions, converted into salts, and tested as such, in the combined state; but when uncombined they are easily distinguished by a solution of nitrate of silver. Magnesia separates the brown oxide of silver, while alumina has no effect upon the solution of nitrate. If the bases are diffused in water, and to each of them a small quantity of sulphuretted hydrogen and nitro-prusside of sodium are added, the magnesia imparts a pale rose-color to the liquid, and the alumina produces no change whatever.

In the following table, P signifies precipitated, and D dissolved.

If the oxides are presented in a solid form, their physical properties will serve in a great measure to identify them. It may be assumed, however, that they are dissolved in water. In this case the solution will have a strong *alkaline reaction,* and nitrate of silver will give with all of them a precipitate of *brown oxide of silver.*

Not P. by Carbonate of Potassa.

	KO	NaO	LiO
	P. by chloride of platinum.	Not P. by chloride of platinum.	
Colors to flame of alcohol.	Lilac.	Yellow.	Crimson.

P. by Carbonate of Potassa.

BaO	SrO	CaO
P. by sulphuric acid.		Not P. by sulphuric acid.
Rapidly.	Slowly.	

Oxalic Acid.

	BaO	SrO	CaO
	P. soluble.	P. insoluble.	
Colors to flame.	Greenish-yellow.	Red.	Orange-red.

SALTS.—The following table refers to the qualitative analysis of the soluble salts of the following bases: KO,NaO,NH_3,LiO,BaO,SrO,CaO,MgO, Al_2O_3. Many of these are neutral: some have an acid and others an alkaline reaction. All are fixed at a high temperature, excepting those of ammonia; hence an ammoniacal salt is excluded, after the dry residue of evaporation has been strongly heated. For the purposes of this analysis, it is assumed that the salt is dissolved in water.

Not P. by Carbonate of Potassa.

KO,NaO,NH_3,	LiO
	P. on boiling if concentrated.

P. by Chloride of Platinum.

KO	NH_3
1. Salts fixed by heat.	1. Salts volatile.
2. Lilac flame to alcohol.	2. Boiled with KO, ammonia evolved.

Not P. by Chloride of Platinum.

	NaO	LiO
	Not P. by alkaline phosphate and ammonia.	P. by alkaline phosphate and ammonia on boiling.
Color to flame of alcohol.	Yellow.	Crimson.

P. by Carbonate of Potassa.

BaO,SrO,CaO	MgO	Al_2O_3
	D. by NH_4Cl. Not D. by KO.	D. by KO. Not D. by NH_4Cl.

Sulphate of Lime.

BaO	SrO	CaO
Precipitated.		Not P.

Chromate of Potassa.

BaO	SrO	CaO
P.	P. only if concentrated.	Not P.

Oxalic Acid.

BaO	SrO	CaO
Not P.	Precipitated.	

Hyposulphite of Lime.

BaO	SrO	CaO
P.	Not precipitated.	

Solution of Ammonia.

	BaO	SrO	CaO	MgO	Al_2O_3
	Not precipitated.			Precipitated.	
Color, to flame of alcohol.	Greenish-yellow.	Red.	Orange-red.	P. soluble in chlor. ammonium. Not D. by KO.	P. insoluble in chlor. ammonium. D. by KO.

The salts of magnesia and alumina impart no color to the flame of alcohol. When strongly heated in the blowpipe flame with a solution of nitrate of cobalt, magnesia acquires a pale-red color, and alumina a bright-blue color. In the compound sulphates of magnesia and alumina with potassa and soda, the peculiar colors given by these alkalies to flame announce their presence.

It will be observed, in considering these groups, that the alkalies are linked to the alkaline earths by lithia, and the alkaline earths to the earths by magnesia. Thus carbonate of lithia may be precipitated from the concentrated solutions of that alkali by carbonate of potassa or soda; but the carbonate of lithia is at the same time sufficiently soluble in water to throw down carbonates of baryta, strontia, and lime from the salts of these bases. The phosphate of lithia occupies also this intermediate position, in respect to solubility. Magnesium and its oxide (magnesia) approach closely to aluminum and alumina in properties. Magnesium is not oxidized by exposure to air: it does not decompose water. It forms one oxide, which is nearly insoluble in water. Its salts are precipitated by ammonia and lime-water. No sulphide of the metal can be obtained by boiling its oxide with sulphur, and no chloride by digesting its oxide in hydrochloric acid, and evaporating to dryness. In these respects the resemblances to alumina, and the differences from the bases with which magnesia is usually associated, are very remarkable.

In dealing with a mixture of the salts of the first and second groups, carbonate of ammonia may be selected as the precipitant. If this reagent, mixed with a small quantity of ammonia and chloride of ammonium, is added to the liquid, and the liquid is warmed, baryta, strontia, and lime only will be precipitated. The filtrate will contain potassa, soda, and magnesia. The latter may be precipitated by adding phosphate of ammonia. When this is separated by filtration, potassa and soda will remain in the filtrate. This is evaporated to dryness, and sharply heated: all the surplus ammoniacal salts are driven off, and salts of potassa and soda only remain for subsequent testing. The base of the third group (alumina) is precipitated with the alkaline earths by carbonate of ammonia. Alumina may be removed from the alkaline earthy carbonates by a solution of potassa.

CHAPTER XXIX.

IRON (Fe=28).

Iron is found largely diffused in the state of oxides and carbonates; it is also found combined with sulphur, and with several acids, and is a common component of many minerals. It occurs in small quantity in some animal and vegetable bodies, and mineral waters, and it forms the principal component of many meteoric stones. (*See* Nickel.)

Manufacture of Iron.—The argillaceous iron ore of the coal-measures is the principal source of British iron. It occurs in nodules and seams, alternating with coal, shale, and limestone, and contains from 70 to 80 per cent. of carbonate of iron, the remainder being chiefly clay and carbonate of lime. It is first roasted, either in kilns or heaps, and, mixed with coke and limestone, is subjected to the intense heat of the blast-furnace; these materials being successively thrown in from the top, and gradually descending till they reach the lower or hottest part. In their descent the iron is reduced, and in combination with a portion of carbon, falls through the fused slags to the bottom of the furnace, whence it is withdrawn at intervals, by opening the *tap-hole*, while the slags are allowed to run off by an aperture left for the purpose: they consist chiefly of the silicates of lime and alumina, with smaller proportions of the silicates of magnesia, manganese, and iron.

The smelting furnaces are usually about 50 feet high, and 15 feet in the widest part of their internal diameter; they are constructed of strong masonry and brickwork, and lined with the most refractory fire-stone. They are worked day and night for several successive years, air being supplied to them by powerful blowing machines, generally so constructed as to throw it in in a heated state, or as a *hot blast*, and to the amount of about six tons weight per hour. It is estimated that by the use of hot instead of cold air, a very large saving of fuel is effected. With the cold blast, about eight tons of coal are consumed in the production of a ton of iron; whereas with the hot blast, less than three tons are sufficient, and with it, coal may be substituted for coke. These furnaces are usually tapped night and morning, furnishing from eight to ten tons of metal daily, and requiring an hourly supply of about a ton and a half of the mixture of roasted ore, limestone, and coal or coke. The melted metal is suffered to run into rough moulds of sand, and in this state constitutes the *cast* or *pig iron* of commerce.

There are several varieties of cast iron, but they are commercially distinguished as 1. *gray*, 2. *mottled*, and 3. *white*. They are all *carbides*, and the gray and mottled varieties include a portion of graphite diffused through them, which remains undissolved and unchanged after the action of dilute sulphuric acid, and, whilst the greater part of the combined carbon unites to the hydrogen, forming hydrocarbons. Cast iron also contains silicon, phosphorus, manganese, and traces of calcium, aluminum, and sulphur.

Gray cast iron is soft and somewhat tough; it admits of being bored, and turned in the lathe. When immersed in dilute hydrochloric acid it leaves a black insoluble residue; its texture resembles bundles of small needles. *Mottled iron* is coarser grained, and small particles of graphitic carbon may be discerned in its fracture. *White cast iron* is very hard and brittle; acids act but slowly upon it, and develop a lamellar rather than a radiated texture: it sometimes contains as much as 5 per cent. of carbon, so that it is nearly represented by Fe_4C, and may be regarded as iron saturated with carbon.

When small articles of cast iron are bedded in oxide of iron (powdered hæmatite is generally used), and kept for some hours at a red heat, they are to a great extent *decarbonized*, and so far softened as to resemble wrought iron, especially when they are slowly cooled. In this operation the carbon of the bar of cast iron appears to be gradually removed, in the form of carbonic oxide, at the expense of a part of the oxygen of the oxide in which they are imbedded.

Wrought, or *malleable iron* is the metal in a comparatively pure state, though it retains traces of carbon and of some of the other impurities of cast iron. To effect the conversion of cast into wrought iron, the cast metal is in the first instance *refined*, by subjecting it to the action of air at a very high temperature, in a kind of forge furnace; much of the carbon is thus burned off; and the silicon, converted into silica, forms a fusible slag with the oxide of iron, which tends to the further purification of the mass. The fused metal is then run off, and formed into cakes, which are rapidly cooled by the affusion of water. The silicate of iron formed in this process is partly derived from the rough cast iron, and partly from added sand; it approaches the composition $3(FeO)SiO_3$, and itself performs a part, in cleansing the metal, by acting as an oxidizing agent. The further, and final purification of the metal, is effected by a process called *puddling*, carried on in a reverberatory furnace, which admits of the fusion of the refined iron by a current of intensely heated air and flame, without direct contact with the fuel; here the metal is well stirred, so that the superficial oxide may be mixed in the mass, which soon begins to heave and emit jets of carbonic oxide, and gradually growing tough and less fusible, becomes at length pulverulent; the fire is then urged so that the particles again agglutinate at a welding-heat, and admit of being made up into globular masses, or *blooms*, and in that state of intense heat are subjected to the *shingling-press*, or to *rollers* by which extraneous matters are squeezed out in the form of slag, and the density of the metal increased; it now admits of being rolled into bars, which are cut into convenient lengths, placed in parcels in a very hot reverberatory furnace, and again rolled. The metal is now tough, flexible, and malleable, but less fusible, and is, in fact, nearly pure, retaining not more than one two-hundredth part of carbon, and mere traces of other matters.

The slags formed in the operations of refining and puddling, containing about 60 per cent. of iron, are reduced in the blast furnace, in the same way as the original ore, but the iron so produced is *cold short;* it admits of working at a red-heat, but is brittle when cold, a quality supposed to depend upon the presence of phosphide of iron, derived from phosphate of iron existing in the slag. Iron is also occasionally *red short*, that is, brittle at a red heat, though malleable when cold; this quality has been ascribed to traces of arsenic and copper.

The quantity of cast iron annually manufactured in Great Britain is of course liable to considerable fluctuation, but it may be estimated at an average of about 3,000,000 tons.

Properties.—Iron is fusible at a white heat, but with great difficulty when perfectly pure. It requires the highest heat of a wind-furnace to run down soft iron nails into a button, and therefore a temperature equal to about 3300°. Its sp. gr. is 7·8. Its texture varies with the method of working; in bars or wires it appears longitudinally fibrous, but when long kept at a red heat it acquires a crystalline texture, and a tendency to cuboidal fracture. It is the hardest and toughest of the ductile metals; it may be drawn into fine wire, but cannot be hammered out into thin leaves; it is very tenacious; and at a bright-red or orange heat it admits of being *welded*, or joined by hammering, to another piece of the red-hot metal. It is attracted by the magnet, but does not retain magnetism when pure; at a bright-red heat it becomes indifferent to it, but reacquires this property on cooling.

To obtain pure iron, filings of the best bar-iron are mixed with about one-fifth their weight of pure peroxide of iron, and exposed (covered with pounded glass quite free from lead) in a well-closed crucible, for about an hour, to the strongest heat of a forge. Exposed to heat and air, iron becomes superficially converted into a fusible oxide; when exposed to a damp atmosphere, it becomes incrusted by a brown *rust*. When in a state of extreme division its affinity for oxygen is such, that it heats, and even ignites, on exposure to air; this is the case with the metal as obtained by the action of hydrogen upon red-hot oxide of iron, and when thus reduced, at a temperature not sufficient to cause the adhesion of the particles of the metal, and suffered to cool in an atmosphere of hydrogen, it requires the same precautions for its preservation as potassium. A spontaneously combustible form of iron is also obtained by the ignition of Prussian blue. In a dense mass, iron is not affected by dry air, and it even retains its polish when immersed in pure water which has been deprived of air; but in common water, or in water exposed to air, it soon rusts. This oxidizement by water is prevented by the alkalies; and in lime-water, or in a weak solution of ammonia, potassa, or soda, the metal keeps its lustre.

OXIDES OF IRON.—Iron is susceptible of four definite degrees of oxidizement—forming a *protoxide* (FeO), which has not been isolated, but which is the bases of a series of well-defined salts; a *sesquioxide* (Fe_2O_3,), generally termed *red oxide* or *peroxide;* a *black* intermediate oxide, known also under the name of *magnetic oxide* (Fe_3O_4); and a *hyperoxide*, called *ferric acid* (FeO_3), but which, like the protoxide, has not been isolated.

PROTOXIDE OF IRON; FERROUS OXIDE (FeO).—When a solution of potassa is added to a solution of a pure protosalt of iron, every precaution being taken to exclude oxygen, a white precipitate falls, which is a *hydrated protoxide;* it is difficult to wash and dry it under entire exclusion of air; but when this is done, it is pale green, not magnetic, and absorbs oxygen when exposed to air, and is converted into peroxide: it rapidly absorbs carbonic acid, and dissolves in the dilute acids. The salts of this oxide, when crystallized or hydrated, are mostly greenish-blue; but white, or nearly so, when anhydrous. In aqueous solution they have an inky taste, and are very prone to pass into salts of peroxide. The fixed alkalies throw down this oxide as hydrate. With ammonia, only half the oxide is precipitated, and a green solution is formed, which, on exposure, becomes covered with a brown film. Carbonates of potassa and of soda, and sesquicarbonate of ammonia, throw down a white protocarbonate of iron, which soon becomes brown, and which, if solution of sal-ammoniac be added, is redissolved. Bicarbonates of potassa and soda produce the same precipitate, unless the solution be very dilute, in which case the mixture is clear, but deposits protocarbonate of iron if boiled, and when exposed to air it gradually lets fall hydrated oxide. The protosalts of iron act as powerful deoxidizers. Nitric acid is decomposed by them, and deutoxide of nitrogen is set free, which is dissolved by a portion of protosalt, and forms a dark olive-green solution (p. 157). The protosalt is at the same time converted into persalt. When added to solutions of chloride of gold or nitrate of silver, gold and silver are separated in the metallic state. It deoxidizes a solution of permanganate of potassa; hence, a standard solution of permanganate is used volumetrically to determine the quantity of protoxide in a liquid.

SESQUIOXIDE OF IRON; PEROXIDE OF IRON; FERRIC OXIDE (Fe_2O_3).—When a protosalt of iron is boiled with nitric or nitro-hydrochloric acid, it becomes peroxidized, and on adding ammonia a brown hydrated precipitate falls, which, when washed and ignited, is the sesquioxide. When protosulphate of iron is decomposed by a very high temperature a red powder remains, which is also the peroxide, and which was formerly called *colcothar*, and is used as a red paint, and for polishing glass and metals. The color of peroxide of iron varies according to the mode of its formation and the temperature to which it has been subjected: it is generally a reddish or yellow-brown powder, which acquires a darkened hue by a moderate heat, and is not magnetic. This oxide is a weak base, or what has sometimes been called an *indifferent oxide:* its salts generally have a brown color and an acid reaction; and, when very dilute, their solutions are decomposed by boiling, in which case the acid of the salt combines with the water, and the peroxide or a basic salt is precipitated. In some cases this oxide acts as an acid. It is thrown down from its solutions by ammonia, potassa, and soda, in the form of a bulky brown *hydrate*, and in this state is easily redissolved by acids; but when it has been dried, and exposed to a full red heat for some time, it is difficultly soluble. It is also partly converted into magnetic oxide by losing oxygen, $3Fe_2O_3=2Fe_3O_4+O$. The best solvent for this oxide is the hydrochloric acid. When dried at 212°, it is $2Fe_2O_3+3HO$; at 400° it becomes Fe_2O_3+HO. A temperature exceeding 500° is required to drive off the whole of the water. When produced under exposure to air, it almost always contains traces of ammonia. When precipitated by excess of the fixed alkalies, or their carbonates, it carries down a portion of the alkali, which cannot be entirely removed by washing; and if the alkali be not in excess, the precipitated oxide is not free from the acid, or from a subsalt: hence the necessity of precipitating by excess of ammonia, when the resulting hydrated oxide may be deprived, by heat, both of water and of excess of the precipitant. When certain organic substances are present in solutions of this oxide they prevent its precipitation by the alkalies. This is the case with hot solutions of gelatine, starch, gum, and sugar. Tartaric, citric, and some other acids, produce the same effect. This oxide of iron is reduced by hydrogen at a temperature even below redness. When gently heated with charcoal it is converted into magnetic oxide, and at a high temperature is reduced.

The salts of this oxide are changed into those of the protoxide by adding sulphurous acid or bisulphite of soda, and warming the liquid; or by adding to the warm liquid pure zinc, in which case hydrogen is generated, and the persalt is converted into a protosalt. A standard solution of permanganate of potassa, which is not affected by a persalt, may be employed volumetrically, to determine by the discharge of color the amount of protoxide, and by calculation of peroxide present. Care should be taken that all the sulphurous acid is expelled from the liquid before adding the solution of permanganate. A current of sulphuretted hydrogen will also reduce the persalts to the protosalts, but in this case there is a separation of sulphur.

BLACK OXIDE OF IRON; MAGNETIC OXIDE OF IRON; FERROSOFERRIC OXIDE (Fe_3O_4; or FeO,Fe_2O_3).—This oxide is formed by passing steam over red-hot iron. The scales of iron obtained from the smith's forge, the oxide formed when iron is burned in oxygen gas, and the black powder formed by the action of air on moistened iron filings, and formerly called *Martial Ethiops*, are also allied to this oxide; but in these the protoxide or peroxide may occasionally predominate. A solution of this oxide in hydrochloric acid has the properties of the proto and persalts of the metal.

A *hydrate* of this oxide may be obtained by dissolving equal weights of protosulphate of iron in two separate portions of water, boiling one of them with a sufficiency of nitric acid to peroxidize it, and then mixing it with the other, and pouring the mixture into a solution of potassa or soda, sufficient in quantity and strength to decompose the whole: the precipitate at first consists of a mixture of protoxide and peroxide of iron, but when boiled for a few minutes they combine, and the black oxide falls in the form of a dense crystalline powder, very obedient to the magnet, and readily soluble in hydrochloric and in nitric acid. The salts of this oxide are mixtures of those of the two oxides. *Magnetic iron ore* is a native black oxide.

FERRIC ACID (FeO_3).—Ferric acid is only known in combination with bases: it is one of those acids which cannot be separated without undergoing decomposition. When sesquioxide of iron is mixed with four parts of nitre, and exposed for an hour to a full red-heat in a covered crucible, it forms a deliquescent reddish-brown mass, which should be powdered while warm, and put into a stopped phial; this is *ferrate of potassa:* its solution in water has an amethystine tinge so deep as to be nearly opaque, and gradually evolves oxygen, and deposits sesquioxide of iron; this decomposition is immediate and perfect at 212°. A solution of ferrate of potassa yields red insoluble precipitates in solutions of baryta, strontia, and lime, which are easily decomposed by acids.

Native Oxides of Iron.—These constitute an extensive and important class of ores. They vary in color, depending upon mere texture in some cases; in others, upon the degree of oxidizement. Some are magnetic, and those which contain least oxygen are attracted by the magnet. The following are some of their principal mineralogical varieties: 1. *Magnetic iron ore,* which is generally black, with a slight lustre. It occurs massive and octahedral, and is often powerfully magnetic; its specific gravity is 4·5. It is abundant in Sweden, where it is manufactured into a bar-iron much esteemed for making steel. 2. The *specular* and *micaceous iron ore.* It is found crystallized, of singular beauty, in Elba, and occasionally among volcanic products. Its specific gravity is 5·0 to 5·2; it yields a reddish powder. 3. *Hæmatite,* or red ironstone, occurs in globular and stalactitic masses, having a fibrous and diverging structure. It is sometimes cut into instruments used for burnishing; its density is 4·8 to 5. It abounds in Lancashire. Sometimes it is of a brown, black, or ochraceous color. This, as well as the iron-glance, is a sesquioxide, and does not affect the magnet. There are also several varieties of *hydrated peroxide of iron,* such as the fibrous hæmatite, the granular and pisiform iron ore, and certain varieties of ochre and umber. 4. A fourth variety of oxide of iron is known under the name of *Bog ore,* found in low marshy places, and generally of recent origin.

IRON AND CHLORINE.—There are two chlorides of iron, corresponding in composition to the protoxide and sesquioxide.

PROTOCHLORIDE OF IRON ($FeCl$) may be obtained by passing dry hydrochloric acid gas over red-hot iron wire; or by digesting iron filings in hydrochloric acid, in which case, as in the former, hydrogen is set free; or by employing protosulphide of iron instead of metallic iron, when sulphuretted hydrogen is evolved; in both cases a green solution is obtained, which, evaporated out of the contact of air, leaves a residue which is to be exposed to a red heat. Protochloride of iron is of a gray color, and after fusion acquires a foliated crystalline texture; it is volatile at a high red heat, and may be condensed in pale gray crystals. When heated with access of air, sesquichloride of iron sublimes, and peroxide of iron remains ($6FeCl+3O=2[Fe_2Cl_3]+Fe_2O_3$). When the vapor of water is passed over it at a dull red heat, hydrochloric acid and hydrogen are evolved, and black magnetic oxide remains: ($3FeCl+4HO=Fe_3O_4+3HCl+H$).

Hydrated Protochloride of Iron.—Dissolved in water free from air, and evaporated *in vacuo,* this chloride furnishes a crystallizable hydrate. When a saturated solution of iron in hydrochloric acid is evaporated, air being excluded, it yields blue rhombic crystals, which become green and effloresce in dry air, into a white powder. Their formula is $FeCl,4HO$. They are soluble in alcohol, and when heated in the air, leave peroxide.

PERCHLORIDE OF IRON; SESQUICHLORIDE OF IRON (Fe_2Cl_3).—When fine iron wire, heated to redness, is introduced into a bell-jar of chlorine, it burns with a lurid red light, and this compound is formed. A mixture of equal weights of chloride of calcium and calcined sulphate of iron, heated to redness, also affords a sublimate of sesquichloride. Sesquichloride of iron forms brilliant and iridescent brown crystals, volatile at a temperature below redness.

Hydrated Sesquichloride of Iron.—Sesquichloride of iron is deliquescent and very soluble in water; when the solution is evaporated in the air, hydrochloric acid passes off, and peroxide of iron remains. A solution of this chloride is obtained by dissolving peroxide of iron in hydrochloric acid; it forms a deep brown liquid, which, when concentrated and exposed to cold, yields crystals, the form of which varies with their respective quantities of water: when they form acicular and radiating tufts, they include about 40 per cent. of water, being $Fe_2Cl_3,12HO$; but when they form larger tabular crystals, they contain about 22 per cent., and are $Fe_2,Cl_3,5HO$; these latter are best obtained by placing the former over a surface of oil of vitriol under a bell-glass; they deliquesce into a thick fluid, which gradually passes into a mass of the crystals containing 5 atoms of water. When a current of chlorine is passed through a solution of protochloride of iron, or when nitric acid is gradually added to it when heated, it is converted into sesquichloride. If a dilute solution of the protochloride be exposed for some days to the atmosphere in a tall jar, and a few drops of ammonia be then introduced at different depths, by means of a glass tube, the precipitate near the surface will be green; a little lower, blue; still lower, gray; then of a dirty white; and, at the bottom, quite white, provided the solution has not been so long exposed as to have become oxidized throughout. The sesquichloride is soluble in alcohol and ether.

AMMONIO-CHLORIDES OF IRON.—Protochloride of iron absorbs ammonia and forms a bulky white powder, which is resolved by water into hydrochlorate of ammonia and hydrated oxide of iron. If iron filings are boiled in a saturated solution of sal-ammoniac, hydrogen and ammonia are evolved, and the liquor deposits green crystals of *hydrated protochloride of iron and ammonia.* When sesquichloride of iron is exposed to ammonia it is slowly absorbed, and the compound furnishes a clear red solution with water; it contains about 9 per cent. of ammonia, being (NH_3,Fe_2Cl_3). A mixed solution of sal-ammoniac and sesquichloride of iron evaporated *in vacuo* over oil of vitriol, furnishes brown crystals, which are $=(2NH_4Cl,Fe_2Cl_3,2HO)$. When hydrochlorate of ammonia and sesquioxide of iron are mixed and heated, a yellow sublimate is obtained, which is the *Ferri ammonio-chloridum* of pharmacy.

PROTIODIDE OF IRON (FeI) is formed by digesting iron turnings, or wire, with iodine in water, taking care to have excess of metal present; a green solution is obtained, which, by evaporation out of contact of air, leaves a gray fusible protiodide of iron. It is soluble in water and alcohol, but the solution absorbs oxygen and deposits peroxide, unless metallic iron is present; so that to preserve it unchanged some pieces of clean iron wire should be immersed in it. By careful evaporation *in vacuo* crystals of a hydrated protiodide of iron, including 5 atoms of water, may be obtained. This salt is used medicinally, and its oxidation is prevented by mixing it with syrup. It is employed in the production of iodide of potassium. There is also a *Bromide* of iron ($FeBr$).

NITRATES OF IRON.—*Protonitrate.*—This compound is formed by digesting iron filings on very dilute nitric acid (specific gravity 1·16). But little gas is evolved, and the liquid assumes an olive-brown color from the nitric oxide which it contains, but when exposed to the air it becomes pale-green in consequence of the escape of this gas. Alkalies produce a green precipitate in this solution; the salt cannot be obtained in crystals by the usual process, and passes into pernitrate by exposure to air. It may, however, be crystallized by evaporation in an exhausted receiver over sulphuric acid; it then forms crystals of a light green color=$FeO,NO_5,7HO$. When protosulphide of iron is dissolved in dilute nitric acid sulphuretted hydrogen escapes, and a green solution of protonitrate is obtained, which, when gently heated, speedily becomes brown, in consequence of the formation of peroxide. Protonitrate of iron is also formed when solutions of protosulphate of iron and nitrate of baryta are mixed in atomic proportions. The solution of the neutral protonitrate is decomposed near the boiling temperature, with the evolution of nitric oxide, and the abundant precipitation of a subnitrate of the peroxide. Iron turnings may be dissolved in cold and highly concentrated nitric acid, so as to produce ammonia and protonitrate of iron, without the extrication of gas ($8Fe, + 10NO_5 + 4HO = 8[FeO,NO_5] + NH_4O,NO_5$).

Pernitrate of Iron; Sesquinitrate of Iron.—Nitric acid, diluted with a little water, acts violently on iron and peroxidizes it; a large quantity of gas is generated, consisting of nitrous and nitric oxides, and a solution is formed of a reddish-brown color, containing *pernitrate* of iron, and affording a brown precipitate with the alkalies. When this solution is evaporated, a brown deliquescent mass remains, soluble in water and alcohol; it is decomposed at a red-heat, and peroxide of iron remains. If this solution be mixed with excess of carbonate of potassa, the precipitate at first thrown down is redissolved by the alkali, and a deep-brown liquid obtained (*Liquor ferri alkalini*).

Passive condition of Iron, in respect to the action of Nitric Acid.—In ordinary cases nitric acid of the specific gravity 1·35 acts powerfully upon iron, but under certain circumstances the metal becomes inert. This state is brought about: 1. By slightly oxidizing the extremity of an iron wire by holding it in the flame of a spirit-lamp, and when cold dipping it gradually into the acid, taking care to introduce the oxidized end first. 2. By dipping the end of the wire into strong nitric acid, and washing it in water. 3. By first introducing a platinum wire into the acid, and then the iron wire in contact with it, which contact may, however, afterwards be broken. 4. An iron wire already rendered passive acts as the platinum wire, and renders other wires passive in the same way.

PROTOSULPHIDE OF IRON (FeS).—When sulphur is dropped upon red-hot iron wire, or fused with iron filings, a compound is obtained, which, after having been heated to expel excess of sulphur, is soluble in dilute sulphuric acid, with the evolution of sulphuretted hydrogen, and is a protosulphide of iron. So also, when a bar of wrought iron is heated nearly to whiteness, and the surface is rubbed with a roll of sulphur, the protosulphide melts from the surface of the metal, and may be collected in a vessel of cold water. It should be perfectly dried. Protosulphide of iron is of a dark-bronze color, and influences the magnet. It is much more fusible than iron; it loses no sulphur, even at a white heat, out of contact of air; when pure, it is soluble without residue in dilute acids, with the evolution of sulphuretted hydrogen and the formation of a protosalt of iron. It is much employed, with diluted sulphuric acid, for the purpose of obtaining sulphuretted hydrogen gas. When heated in air or oxygen, sulphurous acid and oxide of iron are formed. When the moist hydrated protosulphide is exposed to air, the iron becomes oxidized, and sulphur separates, and more or less sulphurous and sulphuric acids are often formed with heat enough to produce inflammation. The formation of this sulphide, by the action of sulphuretted hydrogen upon hydrated peroxide of iron, has already been mentioned (p 212).

BISULPHIDE OF IRON (FeS_2) is formed when the protosulphite is well mixed with half its weight of sulphur, and subjected to a high temperature, which, however, should be below redness; a bulky dark-yellow metallic powder is the result, not attracted by the magnet, and insoluble in dilute sulphuric and hydrochloric acids. Bisulphide of iron is the occasional result of the slow decomposition of a solution of sulphate of iron by organic matter. Thus, the bones of some mice, which had accidentally fallen into a solution of the sulphate, were found incrusted with bisulphide. Its presence in masses of wood found in clay, or in coal, may be explained upon similar principles.

Native Sulphides of Iron.—*Magnetic pyrites* is a protosulphide of iron, and *common* or *yellow pyrites* a bisulphide. Common pyrites is found massive, and crystallized in a variety of forms; it often occurs in radiated nodules, which, when rolled amongst the shingles upon the sea-beach, are sometimes called *thunder-bolts;* it is of different shades of brass yellow. It is used in the formation of *sulphate of iron,* or *green vitriol,* for which purpose it is gently roasted and exposed to air and moisture. The cubical bisulphide is very permanent, but some of the prismatic varieties spontaneously pass into sulphate, and when in large masses generate heat enough to produce ignition; in this way beds of coal have been set on fire in consequence of the absorption of oxygen by their contained pyrites. Pyrites has also been used as a source of sulphur, and as a substitute for sulphur in the production of sulphuric acid.

SESQUISULPHIDE OF IRON (Fe_2S_3).—This compound is formed either by passing sulphuretted hydrogen over sesquioxide of iron at a temperature not exceeding 212°, or by the action of the same gas upon the hydrated sesquioxide, at common temperatures. It is formed in the humid way by adding neutral persulphate of iron drop by drop, to a solution of an alkaline hydrosulphate; it then falls as a black powder, which cannot be dried in the air without change.

HYPOSULPHITE OF PROTOXIDE OF IRON (FeO,S_2O_2) is obtained together with sulphite, by digesting finely-divided metallic iron in sulphurous acid, ($2Fe+3SO_2=FeO,S_2O_2+FeO,SO_2$). When sulphuric or hydrochloric acid is added to its solution, sulphurous acid is evolved, and sulphur precipitated. This solution furnishes a perfect protosalt of iron; and by keeping a few filings of iron in it, it may be retained in this state. It gives a white precipitate with ferrocyanide of potassium, and infusion of galls does not immediately discolor its solution.

PROTOSULPHATE OF IRON (FeO,SO_3) is the *copperas* and *green vitriol* of commerce, and is often prepared by exposing roasted *pyrites* to air and moisture, in which case the salt is impure. It is usually formed by dissolving iron in dilute sulphuric acid, filtering and evaporating the solution, and setting it aside to crystallize. It is also obtained, free from persulphate, by acting upon *protosulphide* of iron by dilute sulphuric acid. This salt forms, when pure, bluish-green crystals in the form of oblique rhombic prisms, soluble in about 2 parts of water at 60°; of a styptic taste, reddening vegetable blues, and including 7 atoms of water ($FeO,SO_3 7HO$). When chlorine is passed through an aqueous solution of protosulphate of iron, hydrochloric acid is formed, and the iron becomes peroxidized, so that water is decomposed. Protosulphate of iron is insoluble in alcohol, and in sulphuric acid, both of which deprive the crystals of water, and precipitate the salt in the form of a white powder. The green vitriol of commerce usually contains persulphate, and has a grass-green color. Exposed to dry air, this salt effloresces, and in moist air absorbs oxygen, becoming of a rusty or reddish color, whence the French term *couperose,* applied to it, corrupted into *copperas.* When heated in close vessels, it fuses, and at 238° loses 6 equivalents of water, but retains 1 equivalent till heated above 535°: this may be driven off at a higher temperature, and the salt is then white, pulverulent, and anhydrous. At a higher temperature the anhydrous protosulphate is converted into an anhydrous persulphate, and sulphurous acid is at the same time evolved: $2[FeO,SO_3]=Fe_2O_3,SO_3+SO_2$; and at a full red-heat the persulphate is itself decomposed, and leaves peroxide, while the sulphuric acid partly passes off in an anhydrous state, and is partly resolved into sulphurous acid and oxygen. The residuary oxide is of a deep-red color, and was formerly known under the name of *colcothar*, or *caput mortuum vitrioli*. It is in consequence of this decomposition that sulphate of iron is often used as a substitute for sulphuric acid, to separate weaker acids from their bases, at high temperatures.

Native Green Vitriol is frequently found associated with pyrites, and produced by its decomposition.

PERSULPHATE OF IRON ($Fe_2O_3,3SO_3$) is made by adding 1 equivalent of sulphuric acid to a solution of 2 equivalents of protosulphate, boiling, and then dropping in nitric acid as long as red fumes are evolved; a buff colored deliquescent mass is obtained on evaporation, slowly soluble in water, and which, when carefully heated, leaves an anhydrous salt: it is decomposed at a red heat. In this compound the number of atoms of acid are equal to the number of atoms of oxygen combined with the metal.

Persulphate of iron forms double salts with the sulphates of ammonia and of potassa, which, in form and composition, resemble alum. The formula of the ammonia-salt is $NH_4O,SO_3+Fe_2O_3,3SO_3+24HO$, and that of the potassa-salt $KO,SO_3+Fe_2O_3,3SO_3+24HO$. It is sometimes found associated with sulphate of alumina in chalybeate waters.

PHOSPHIDE OF IRON (Fe_4P) is formed by dropping phosphorus into a crucible containing red-hot iron-wire: it is a brittle gray compound, and acts upon the magnet. It may also be procured by the ignition of a mixture of iron filings, phosphoric acid, and charcoal powder; or of phosphate of iron and charcoal. It is difficultly soluble in the acids. A small portion of this compound is said to be present in *cold-short iron:* it is injurious to the quality of the metal when contained in it to the amount of 1 per cent. Phosphorus increases the fusibility of iron. The fine thread-like Berlin castings are said to be produced from iron containing the phosphide.

PROTOPHOSPHATE OF IRON ($2(FeO)HO,PO_5$) is insoluble in water. It may be formed by adding a solution of common phosphate of soda to protosulphate of iron. It is at first white, but becomes blue by exposure: it fuses and forms a crystalline bead before the blowpipe; it is soluble in most of the acids, from which it may be again precipitated by ammonia, but it is soluble in excess of ammonia. When it has acquired a full blue tint, it is probably analogous to the *native phosphate*, and is a hydrated compound of the phosphate of the protoxide with phosphate of the peroxide. This blue phosphate may be produced by adding phosphate of soda to the solution of the mixed sulphates of iron; it is not changed by exposure to air; its formula is $HO,2(FeO)PO_5+2(Fe_2O_3)PO_5$. The analyses of the crystallized and amorphous native phosphates agree with the formula $3(FeO)PO_5+8HO$.

PERPHOSPHATE OF IRON is a white insoluble compound which is precipitated on adding common phosphate of soda to persulphate or perchloride of iron; or by adding phosphoric acid to a mixture of acetate of soda and a persalt of iron. The precipitate is rendered brown by solution of ammonia, but is not soluble in ammonia unless excess of the phosphate of soda is present, when it forms a brown solution, which remains clear with ferrocyanide of potassium till an acid is added, when Prussian blue is thrown down. It is also dissolved by a large excess of peracetate of iron. Owing to the insolubility of the perphosphate in acetic acid, an alkaline phosphate forms a valuable test for this metal (page 368), and enables a chemist to separate iron from the alkaline earths, as well as the peroxide from the protoxide of the metal.

Native Phosphate of Iron occurs in the form of a blue earthy powder; or if at first white, it becomes blue by exposure: it also is found in prismatic crystals. The former (sometimes termed *Native Prussian Blue*) has been found in alluvial soil: the latter occurs with iron pyrites in Cornwall.

IRON AND CARBON. CARBIDE OF IRON.—It is doubtful how far any definite carbide of iron can be separately obtained, but these compounds have important bearings upon the properties of cast iron and steel. The determination of the quantity of carbon in them is usually effected by mixing from 50 to 100 grains of the sample in very fine filings, with about ten times its weight of chromate of lead, heating the mixture in a combustion-tube, such as is used in organic analyses, to a red-heat, and passing over it a stream of pure and dry oxygen: in this way the iron and carbon are both burned, and the carbonic acid formed by the latter, when absorbed by a solution of potassa, becomes the indicator of the quantity of carbon present. But cast iron contains carbon mechanically mixed, as well as chemically combined; and to ascertain their relative proportions, the iron may be dissolved in hydrochloric acid, when the chemically combined carbon goes off in the form of *hydrocarbons*, while the graphite, or other forms of carbon, which were mechanically mixed, remain, together with silica, and may be separated by filtration, washed, and dried. This residue, when properly burned, so as to consume the carbon, leaves the silica, and the loss of weight gives the quantity of carbon.

Manufacture of Steel.—Steel is generally regarded as a compound of iron with a quantity of carbon, varying from one to two per cent.; but the exact nature of this valuable substance is perhaps scarcely understood. In some samples the proportion of carbon has been found below 0·2 per cent.; in others, nitrogen has been detected; and under the supposition that these small quantities of foreign matters cannot confer upon steel the remarkable properties upon which its value depends, it has been assumed that it may be an allotropic condition of iron. Traces of silicon, manganese, phosphorus, arsenic, and aluminum, have also been discovered in steel of good quality.

Steel combines the fusibility of cast, with the malleability and ductility of bar or wrought iron; its texture varies, some of the varieties being granular or lamellar, and others exhibiting a silky fracture; but it is never fibrous, like the iron from which it is obtained. After it has been highly heated, and then suddenly cooled, it acquires extreme hardness, and becomes more or less brittle, and very elastic; but if, after having been heated to redness, it be allowed to cool very slowly, it becomes nearly as tough and soft as pure iron. But the most characteristic quality of steel is, that it may be brought to any intermediate degree of hardness between these extremes, by the process called *tempering*, to which we shall presently advert. Steel is also distinguished from iron by its permanent retention of magnetism. Steel may be obtained from the purer varieties of cast-iron, or from some of the native oxides of iron, by so modifying the process of reduction as to leave the iron in combination with no more carbon than is requisite; and, in that case, it has been termed *natural steel*. Iron may also be converted into steel by passing carburetted hydrogen over the bars at a full red heat; but it is generally made by a process called *cementation*, which consists in heating to full redness, bars of the purest iron, in contact with charcoal, to which a little common salt and wood-ash is usually added. This process requires from 6 to 10 days, according to the thickness of the iron bars, which, when removed from the furnace, exhibit a *blistered* surface, arising, as has been supposed, from the production of carbonic oxide. When *blistered steel* is drawn down into smaller bars, and forged by the tilt hammer, it forms *tilted steel;* and this, when broken up, and again welded and drawn into bars, forms *shear steel. Cast steel* is prepared by fusing blistered steel with a carbonaceous and vitrifiable flux, and casting it into ingots, which are afterwards hammered or rolled into bars. It has a more uniform texture and composition than the other varieties, and is used in the manufacture of superior cutlery, and for the matrices, punches, and dies of the medal engraver and coiner.

The best cast steel seldom contains less than 99 per cent. of iron, the remaining 1 per cent. being made up of carbon, silicon, phosphorus, manganese, and occasional traces of the other substances found in cast iron.

Case-hardening is an operation performed upon cast or wrought-iron, by which it is superficially converted into steel: the article is for this purpose either heated to redness in contact with charcoal-powder; or sometimes, if small and delicate, is wrapped round with leather, and then gradually heated to redness, and kept in that state till its surface is duly carbonized. Ferrocyanide of potassium is also a valuable material as a case-hardener, and in various operations connected with the management of steel.

Hardening and Tempering Steel.—When steel is heated to a cherry-red color, and then plunged into cold water, it becomes so extremely hard and brittle, as to be unfit for almost any practical purpose. To reduce it from this extreme hardness it is subjected to the process of *tempering*, which is effected by again heating the steel up to a certain fixed point. The surface being a little brightened, exhibits, when thus heated, various colors depending upon the formation of thin films of oxide, which constantly change as the temperature is increased, and by these colors it is customary to judge of the *temper* of the steel. But a more accurate method is to use a bath and thermometer; the bath may be of oil, mercury, or fusible metal. Into this the articles to be tempered are put, together with the bulb of a thermometer graduated to the boiling point of mercury. The corresponding *degrees* at which the various colors appear are from 430° to 600°. The first change is about 430°, but this is very faint. At 460° the color is *straw*, at 500°, *brown;* this is followed by a *red* tinge, then *purple*, and at nearly 600°, it is *blue*. Lancets, certain surgical instruments, and razors, are tempered between 430° and 460°; penknives, and fine cutlery, at 460° to 500°; table and carving-knives at 500° to 530°; and sword-blades, saws, and articles requiring great elasticity, at 530° to 600°.

When a mass of steel, a die, for instance, has been heated red-hot, and suddenly quenched in cold water, it retains when cold, the bulk that it had when heated; the consequence is, that its particles are thrown into a state of very unequal tension, so that it frequently cracks or flies to pieces. Its specific gravity is also diminished. The specific gravity of a plug die of the best cast steel, weighing about 2600 grains, after having been well annealed, was 7·8398; after having been indented by a punch in a fly-press, its specific gravity was 7·8605; it was then hardened by heating it to bright redness and plunging it into water at 55°. By this process its sp. gr. was reduced to 7·7525.

The quality of steel is sometimes tested by washing its clean surface with dilute nitric acid, which ought to produce a uniform gray color; if the steel is imperfect, and contains veins or pins of iron, they become evident by their difference of color. When some particular kinds of iron or steel are thus tested, a mottled appearance is produced, as if it were composed of layers or wires of iron and steel welded together: hence is supposed to arise the peculiar character of the celebrated *Damascus* sword-blades.

Alloys of Steel.—Attempts have been made to improve the quality of steel by alloying it with manganese, silver, and some other metals, but none of these combinations have been found, after due experience, to be superior to the best ordinary steel.

PROTOCARBONATE OF IRON (FeO,CO_2).—When a solution of a pure protosalt of iron is precipitated by carbonate of potassa or soda, a white *hydrated protocarbonate of iron* falls, which, if washed and dried, with all the requisite precautions for excluding oxygen, forms a greenish tasteless powder, containing from 24 to 30 per cent. of carbonic acid; it may therefore be considered as FeO,CO_2,HO. When air is not excluded, the white precipitate presently passes through various shades of green, and if exposed to air becomes brown, losing carbonic acid, and passing into hydrated peroxide. When carbonic acid in aqueous solution is digested with iron filings, a colorless solution of the protocarbonate is obtained. It is not an uncommon ingredient in mineral waters, where it is held in solution by excess of carbonic acid. The most celebrated springs of this kind in England are those of Tunbridge Wells. These waters have an inky flavor, are blackened by vegetable astringents; and when boiled, or when exposed to air, deposit hydrated peroxide of iron. Chalybeate waters seldom contain as much as a grain of carbonate of iron in a pint; the chalybeate springs in and about Tunbridge Wells contain from 2 to 3 grains in the gallon (p. 138).

Native Protocarbonate of Iron, or *Spathose Iron Ore* (FeO,CO_2) occurs in rhombic crystals. Its color is yellowish, or brownish gray. It generally contains manganese, lime, and a trace of magnesia; it slowly dissolves in hydrochloric acid, evolving carbonic acid. The *clay iron ore* of our coal districts, from which British iron is chiefly obtained, is an impure *protocarbonate of iron*, usually containing from 30 to 40 per cent. of oxide (p. 353). Carbonic acid does not form a definite compound with *peroxide* of iron.

IRON AND CYANOGEN.—These substances give rise to several important compounds, in which they exist either combined in various proportions or as a compound radical or base, in union with other bodies.

PROTOCYANIDE OF IRON ($FeCy$) is obtained, in the form of a gray powder, by gently heating ammonio-cyanide of iron (ferrocyanide of ammonium) out of the contact of air. It is also formed by digesting recently-prepared Prussian blue in a well-stopped phial with a saturated solution of sulphuretted hydrogen; it becomes white, and the solution contains hydrocyanic acid. When solutions of cyanide of potassium and protosulphate of iron are mixed, an abundant reddish precipitate falls, which is redissolved by excess of the cyanide, and then forms ferrocyanide of potassium. But it is doubtful whether a *pure* protocyanide of iron has been isolated.

According to Pelouze, a combination of cyanogen and iron (Fe_3Cy_4), corresponding to the magnetic oxide, is obtained by passing a current of chlorine into a boiling solution of ferrocyanide of potassium; a green powder precipitates, which is to be boiled in 8 or 10 parts of concentrated hydrochloric acid, by which peroxide and cyanide of iron are dissolved, and a green powder remains, which, when washed and dried *in vacuo*, constitutes this intermediate combination$=FeCy+Fe_2Cy_3+4HO$. Heated to 355°, it loses water, cyanogen, and a little hydrocyanic acid, and acquires a deep purple color. By a solution of caustic potassa, it is converted into peroxide of iron, and a mixture of the ferrocyanides of potassium.

PERCYANIDE OF IRON; SESQUICYANIDE OF IRON (Fe_2Cy_3).—This compound has not been isolated. It is obtained in solution when ferricyanide of potassium is decomposed by silico-fluoride of iron, forming a brown astringent liquid, but on evaporation it deposits Prussian blue. The varieties of Prussian blue are compound cyanides of iron.

Ferrocyanides and Ferricyanides.—The cyanides of iron combine with other cyanides and produce two classes of salts, which have been termed *ferrocyanides* and *ferricyanides*, the former containing *ferrocyanogen*=$FeCy_3$, and the latter *ferricyanogen*=Fe_2Cy_6. Neither ferrocyanogen nor ferricyanogen has been isolated, but the hypothesis of their existence as distinct radicals is so convenient, as to have led to its general adoption. Ferrocyanogen, Fcy, containing 1 atom of iron and 3 of cyanogen, is *dibasic.* Ferricyanogen, Fdcy, containing 2 atoms of iron and 6 of cyanogen, is *tribasic.* The ferrocyanide of potassium, for instance, is K_2,Fcy, and the ferricyanide, K_3,Fdcy; the ultimate elements of the former being $K_2FeC_6N_3$; and those of the latter, $K_3Fe_3C_{12}N_6$. They are isomeric (p. 19).

FERROCYANIDE OF HYDROGEN; FERROCYANIC ACID; HYDROFERROCYANIC ACID (H_2,Fcy=H_2,Fe,Cy_3).—(*Ferrochyazic acid* of Porret, by whom it was discovered in 1818.)—This acid may be obtained by the following processes: 1. Dissolve 58 grains of crystallized tartaric acid in alcohol, and pour the solution into a phial containing 50 grains of ferrocyanide of potassium dissolved in 3 drachms of warm water; the potassa is precipitated in the state of bitartrate, and the hydroferrocyanic acid remains dissolved in the alcohol, from which it may be obtained, by careful evaporation, in small crystals. 2. Mix a cold saturated solution of ferrocyanide of potassium with one-fourth of its volume of strong hydrochloric acid, and agitate it with half its volume of ether; a white crystalline substance separates, which, when washed with ether and dried, or, if necessary, dissolved in alcohol, and again precipitated by ether, is hydroferrocyanic acid. In this decomposition, 1 atom of ferrocyanide of potassium and 2 of hydrochloric acid yield 1 of hydroferrocyanic acid and 2 of chloride of potassium. Hydroferrocyanic acid thus obtained, is soluble in water and alcohol, and powerfully acid: it decomposes the alkaline carbonates with effervescence, forming ferrocyanides of their bases. It is inodorous, and not poisonous: it is permanent in the dry state, but when moistened and exposed to air it forms Prussian blue.

Ferrocyanogen, regarded as a bibasic radical, forms two sets of salts, combining, namely, with 2 atoms of the same metal, as in the ferrocyanide of potassium, F_2Fcy; or with 2 atoms of different metals, as in the ferrocyanide of potassium and calcium, K,Ca,Fcy; and when these salts are formed by the hydroferrocyanic acid, the 2 atoms of its constituent hydrogen are replaced by 2 atoms of the same or of different metals (p. 230).

The *ferrocyanides* are decomposed by heat with various phenomena. 1. The ferrocyanogen evolves nitrogen and becomes converted into carbide of iron, which remains mixed with the basic cyanide; this is the case with *ferrocyanide of potassium.* 2. The cyanogen of both the cyanides is decomposed, nitrogen evolved, and metallic carbides of iron and of the basic metal are formed; as with *ferrocyanide of lead.* 3. The basic cyanide evolves cyanogen, and is reduced; as in the case of *ferrocyanide of silver.* (*See* p. 195.)

FERROCYANIDE OF IRON.—When ferrocyanide of potassium is added to a pure protosalt of iron, a whitish precipitate falls, which becomes blue by exposure, and is =K,Fe_2,Cy_3. The same salt is thrown down on adding hydrochloric acid to a solution of ferrocyanide of potassium. Representing this salt by the formula KFe,Fcy, it comes under the class of *ferrocyanides with two basic metals.*

Prussian Blue.—This pigment was accidentally discovered by Diesbach, a color-maker at Berlin, in the year 1710. It is largely consumed in the decorative arts, in dyeing, and calico-printing: it is used in making some of the varieties of what is called *stone-blue*, and is sometimes added to starch, though for this purpose, as well as for covering the yellow tint of paper, smalt or cobalt blue is preferable. Prussian blue is prepared of different degrees of purity, by precipitating solutions of peroxide of iron by ferrocyanide of potassium, various additions being made according to the purposes for which it is required.

Pure Prussian blue is obtained by adding a solution of ferrocyanide of potassium to persulphate of iron, thoroughly washing the precipitate, first with water slightly acidulated by sulphuric acid, and then with pure water, and ultimately drying it in a warm place. Prussian blue is of a peculiarly rich and intense blue, with a copper tint upon its surface: it is insipid, inodorous, insoluble in water, in alcohol, and in dilute acids, and is not poisonous. Concentrated sulphuric acid forms with it a white pasty mass by dehydrating it, from which water again separates it as Prussian blue; nitric acid decomposes it; concentrated hydrochloric acid ultimately abstracts part of its iron. Sulphuretted hydrogen, and nascent hydrogen, gradually destroy its color. The alkalies decompose it into soluble ferrocyanides and oxide of iron, hence, as a dyeing material, it does not resist the action of soap. Boiled in water with peroxide of mercury, it forms cyanide of mercury, and an insoluble compound of cyanide and oxide of iron. According to Chevreul, Prussian blue becomes white in the direct rays of the sun, but regains its blue color in the dark. It is occasionally used in the composition of writing fluids. It is hygrometric, and after having been well dried, speedily attracts moisture. When subjected to destructive distillation, it yields a little water with hydrocyanate of ammonia, and then carbonate of ammonia; a black pyrophoric carbide of iron remains.

Prussian blue is regarded as a compound of cyanogen and iron, but various views have been taken of its atomic constitution, according as it has been considered to contain, or not to contain, the elements of water. When anhydrous, it contains 7 atoms of iron and 9 of cyanogen; or 4 atoms of iron and 3 of ferrocyanogen; but it is generally admitted that it cannot practically be obtained in this state, and that it always contains water, or the elements of water, which cannot be expelled without the decomposition of the compound; if so, it is probably a hydroferrocyanate of the sesquioxide of iron.

Ferrocyanide of Potassium and Iron.—It has already been observed that the white precipitate resulting from the action of ferrocyanide of potassium upon a protosalt of iron, contains 1 atom of potassium, 2 of iron, and 3 of cyanogen, and is identical with the salt produced by the action of sulphuric acid upon ferrocyanide of potassium; it is therefore a ferrocyanide, in which 1 atom of potassium is replaced by an atom of iron $=K,Fe_2Cy_3$; or it may be regarded as a compound of 1 atom of ferrocyanide of potassium with 3 of cyanide of iron $=(K_2,Fe,Cy_3+3FeCy=2(K,Fe_2,Cy_3)$. When this white compound is exposed to air, it absorbs oxygen and becomes blue, forming what has been termed *soluble* or *basic Prussian blue*, a compound of Prussian blue with peroxide of iron $=(Fe_7,Cy_9+Fe_2O_3)$. When washed with water, the ferrocyanide is first washed away, but if the washing be continued the whole of the precipitate is gradually dissolved, furnishing a dark-blue liquor, which may be evaporated to dryness without decomposition. The blue liquor is not precipitated by alcohol, but when solution of sulphate of potassa (and certain other salts) is added, a blue precipitate falls, which is again perfectly soluble in pure water.

FERRICYANOGEN (Fe_2Cy_6=Fdcy).—This assumed tribasic salt radical is isomeric with ferrocyanogen, being formed by the coalescence of 2 atoms of that compound.

FERRICYANIDE OF HYDROGEN. *Hydroferricyanic Acid* (H_3,Fe_2Cy_6 or H_3, Fdcy).—This acid is prepared by decomposing recently precipitated ferricyanide of lead by dilute sulphuric acid, or by sulphuretted hydrogen: on filtration a yellow liquor is obtained, which by very slow spontaneous evaporation deposits crystals; if heat be used, a brown powder remains: the aqueous solution gradually decomposes, especially if heated, and deposits a blue crystalline powder. This acid, in combining with metallic oxides, produces water and metallic ferricyanide, its hydrogen being replaced by the metal: its compounds with the metals of the alkalies and alkaline earths are soluble in water; the others are insoluble, and are formed by the reaction of a soluble ferricyanide upon solutions of the metallic salts (pp. 232, 271).

FERRICYANIDE OF IRON ($Fe_5Cy_6 = Fe_3,Fdcy$).—This is the precipitate formed by adding solution of ferricyanide of potassium to a protosalt of iron; it is produced by the substitution of 3 atoms of iron for 3 of potassium; it is known in commerce as *Turnbull's blue* $(K_3,Fdcy)+3(FeO,So_3)=(Fe_3,Fdcy+3KO,SO_3)$. It may also be prepared by adding to a protosalt of iron a mixture of ferrocyanide of potassium and chloride of soda, to which hydrochloric acid has been previously added. It is distinguished from common Prussian blue by its action on ferrocyanide of potassium, for when boiled in a solution of the latter salt it decomposes it into ferricyanide, which is dissolved, and into an insoluble gray residue of ferrocyanide of iron and ferrocyanide of potassium.

HYDRONITROPRUSSIC ACID and *Nitroprussides.*—When binoxide of nitrogen is passed through an aqueous solution of hydroferricyanic acid, one of the products is *hydronitroprussic acid,* the formula of which is H_2,Fe_2Cy_5,NO_2: it forms a well-defined series of salts, discovered by Dr. Playfair (*Phil. Trans.* 1848). One of the most characteristic of these is the *nitroprusside of sodium:* Na_2,Fe_2Cy_5,NO_2+4Aq. It is obtained by the action of 5 parts of nitric acid (diluted with its bulk of water) upon 2 parts of pulverized ferrocyanide of potassium; cyanogen and hydrocyanic acid are evolved, and, when the effervescence has ceased, the solution is heated in a water-bath till it produces a gray (instead of a blue) precipitate with a protosalt of iron: it is then set aside, and crystals of nitre, with some oxamide, are deposited; these being removed, the solution is neutralized by carbonate of soda, which throws down a greenish-brown precipitate, and, on filtering and evaporating the liquid, crystals of the nitroprusside and of the nitrates of potassa and soda are obtained: the former are picked out and purified by another crystallization.

Nitroprusside of sodium forms red prismatic crystals, soluble in about 2½ parts of water. The solution, when exposed to light, deposits Prussian blue, and evolves nitric oxide; when an alkaline sulphide is added to it, even in a most diluted state, it assumes a deep and characteristic purple color, which, however, soon disappears (pp. 272, 367).

Nitroprusside of Barium (Ba_2,Fe_2Cy_5,NO_2+6Aq) forms red octahedral crystals.

ALLOYS OF IRON.—These compounds are not of much importance, except perhaps those of zinc and tin, as far as they are concerned in the production of zinced and tinned iron, which are mentioned under those metals.

TESTS FOR THE SALTS OF IRON. *Protosalts.*—The solutions of these salts have a greenish color, and a peculiar metallic inky taste. 1. Sulphuretted hydrogen gives no precipitate in a solution of a protosalt, provided it is acid. 2. Hydrosulphate of ammonia gives a precipitate of greenish black sulphide, part of which is dissolved, and imparts a green tint to the alkaline liquid. When exposed to the air, this precipitate is converted into a reddish-brown basic salt of the peroxide. 3. *Potassa* and *soda* throw down a white hydrated oxide, insoluble in the alkali. This, by exposure to air, rapidly becomes green, and ultimately brown (hydrated peroxide). When precipitated under similar circumstances, the oxide of manganese becomes brown, but without passing through any shade of green. 4. *Ammonia* gives a similar precipitate, which is partly dissolved by an excess, forming a greenish colored liquid; but on exposure, the solution or precipitate undergoes similar changes. 5. *Alkaline phosphates* and *arsenates* throw down white precipitates (phosphate and arsenate) which pass through similar changes. The precipitated phosphate of the protoxide is soluble in acetic acid. 6. *Ferrocyanide of potassium* gives a white precipitate (p. 365), which, by the rapid absorption of oxygen, acquires a dark blue color (Prussian blue). Hence this white precipitate forms a useful test for free oxygen (p. 90). 7. The *ferricyanide of potassium* gives a rich blue precipitate (p. 272). The precipitates given by this and the preceding test are insoluble in strong hydrochloric acid. If the solution is alkaline, they are not produced, since alkalies decompose them. 8. *Tincture of galls* (tannic acid) produces no change of color in the solutions of pure protosalts, but by the absorption of oxygen, and the oxidation of the protoxide, the liquid soon acquires, on the surface, a pink, purple, blue, or even black tint, according to the quantity of peroxide of iron produced. Sulphocyanide of potassium and succinate and benzoate of ammonia produce no precipitate or change of color.

Persalts of Iron.—The solutions are generally brownish-yellow and very acid. The more neutral they are, the deeper the color. 1. *Sulphuretted hydrogen* gives with the solution a milky-white precipitate of sulphur—the persalt being converted to a protosalt ($Fe_2O_33SO_3+HS=2(FeOSO_3)+HO, SO_3+S$). 2. *Hydrosulphate of ammonia* gives a black precipitate of sulphide of iron (FeS) with a separation of sulphur. This precipitate is soluble in hydrochloric acid. It becomes brown by exposure to air. 3. *Potassa, soda*, and *ammonia*, as well as their *carbonates* and *bicarbonates*, throw down brown hydrated peroxide, insoluble in an excess of the alkalies or their salts, as well as in chloride of ammonium. Some organic substances, if present, will interfere with this action of the alkalies (p. 356). In this case hydrosulphate of ammonia should be employed. 4. *Phosphate* or *arsenate of soda* gives, in a diluted and nearly neutral solution of a persalt, a whitish or pale brown precipitate of phosphate or arsenate of iron, insoluble in acetic acid, but dissolved by mineral acids; this precipitation is promoted by boiling. Peroxide of iron may thus be separated from the alkalies and alkaline earths, as well as from any protoxide of iron which may be present: these bases are held in solution. 5. *Ferrocyanide of potassium* produces, even in a very diluted solution, a blue precipitate (Prussian blue, p. 365) which is insoluble in hydrochloric acid. 6. *Ferricyanide of potassium* gives a deep emerald-green color to the liquid, but no precipitate of Prussian blue is formed. 7. *Sulphocyanide of potassium* gives a blood-red tint even when the persalt is largely diluted. This color is destroyed by heat and by solutions of chloride of gold and corrosive sublimate. 8. *Tincture of galls* (tannic acid) gives immediately a blue-black color, which is destroyed by strong mineral and some vegetable acids. 9. *Succinate* and *benzoate of ammonia* (if the solution is not too acid) throw down pale reddish-brown precipitates (persuccinate and perbenzoate of iron). The protosalts of iron and the salts of manganese are not precipitated by these two reagents.

The protoxide may be separated from the peroxide of iron by various processes. 1. The solution of the two salts, nearly neutralized, may be treated with acetate of soda, and a small quantity of phosphoric acid then added. The perphosphate of iron alone is precipitated, especially when the liquid is boiled, the protophosphate remaining dissolved in the acetic acid. 2. The mixed oxides should be dissolved in the hydrochloric acid, and the liquid warmed. If carbonate of baryta is then added to this liquid in a covered vessel, the hydrated peroxide of iron only is precipitated. On warming the acid liquid, the protosalt is obtained in solution in the filtrate. 3. A solution of permanganate of potassa loses its red color by admixture with the proto, but not with the persalts, hence the proportions of the mixed oxides may be determined volumetrically. Dissolve the oxides in hydrochloric acid and dilute the liquid until it is colorless. A standard solution of permanganate of potassa, of which a certain number of measures correspond to a grain of protoxide, is now added. When the color is no longer discharged, the operation is stopped, and the number of measures, representing grains of protoxide, read off. It has been hitherto the custom to estimate iron by precipitating it by ammonia as peroxide from a persalt. The precipitate is simply washed with warm water, dried, calcined, and weighed. The volumetric method, however, is preferable. If a few zinc filings are placed in the acid liquid, warmed, or a little sulphite or bisulphite of soda is added to it, the persalt is rapidly converted into protosalt, and in this state the proportion present admits of speedy determination by the use of permanganate of potassa. The zinc should contain no iron, and the whole of the sulphurous acid should be removed by boiling. 36 parts of anhydrous protoxide are equal to 40 parts of anhydrous peroxide. Iron may be readily separated, as peroxide, from all the alkalies, as well as from baryta, strontia, and lime, by adding to the acid solution, ammonia and hydrochlorate of ammonia. It may be separated from magnesia, the protoxide of manganese, nickel, and cobalt, by diluting the liquid containing the persalt of iron, and adding a solution of carbonate of soda, until it has acquired a brownish-red color. If acetate of soda is then added and the liquid boiled, the hydrated peroxide of iron is precipitated (WILL). A very delicate test for the presence of a protosalt in a persalt, is to boil the diluted liquid with chloride of gold. If a trace of protosalt is present, metallic gold is deposited.

None of the metals precipitate iron in a metallic state, if we except zinc and cadmium, which effect an imperfect precipitation from some of its protosalts, in vessels excluded from the access of air. Before the blowpipe, peroxide of iron produces with microcosmic salt, or borax, in the exterior flame, a glass which is blood-red while hot, but yellow when cold. The protoxide forms a green glass, which, by increasing the proportion of the oxide, passes through bottle-green to black, and is opaque. The glass from the peroxide which is reddish-colored in the exterior, becomes green in the interior flame: it is there reduced to protoxide, and becomes attractable by the magnet.

The native compounds of iron may be dissolved by hydrochloric or nitrohydrochloric acid. The silicates containing iron should be fused with four times their weight of the mixed carbonates of potassa and soda. The iron then becomes entirely soluble in hydrochloric acid.

CHAPTER XXX.

MANGANESE ($Mn=28$).

THE common ore of manganese is the black, or *peroxide;* it is found in considerable abundance, and is of great importance as a source of oxygen, and for the production of chlorine from seasalt, and as a chemical agent in various arts and manufactures. Manganese also occurs in several mineral compounds, and traces of it are found in the ashes of some plants, in a few animal products, and in some spring waters.

To obtain metallic manganese, carbonate of manganese, mixed into a paste with oil, is subjected to a heat gradually raised to redness, in a close vessel. The carbonaceous mixture thus obtained is then rammed into a good crucible, filled up with charcoal-powder, and submitted for two hours to a white heat: a metallic button is thus obtained, which is manganese, containing a little carbon and silicon, from which it may be freed, by fusion with borax in a crucible coated with charcoal; it is doubtful, however, whether in this case it does not retain boron or sodium. Manganese is a gray metal with a granular or slightly crystalline fracture. Sp. gr. 8·013. It is best preserved in naphtha, for in the air it tarnishes and crumbles into powder; it undergoes the same change in water, with the evolution of hydrogen. When handled with moist fingers, it exhales a disagreeable odor, and when acted on by acids, the purest specimens afford traces of carbon.

MANGANESE AND OXYGEN.—There are five compounds of manganese and oxygen, three of which are oxides, and two acids; together with two intermediate oxides, namely, the red oxide, and the mineral called Varvicite. Their formulæ are as follows:—

Protoxide	MnO
Sesquioxide	Mn_2O_3
Binoxide (Peroxide)	MnO_2
Red oxide (Hausmannite)	Mn_3O_4
Varvicite	Mn_4O_7
Manganic acid	MnO_3
Permanganic acid	Mn_2O_7

PROTOXIDE OF MANGANESE; MANGANOUS OXIDE; (MnO) is obtained by passing a current of dry hydrogen over carbonate of manganese, in a porcelain tube, exposed to a red heat. It should be allowed to cool before removal from the tube, otherwise it is apt to absorb oxygen. It is of a dingy green color; when heated in the air it is converted into sesquioxide; and at a temperature of about 600° burns sometimes like tinder. It is soluble in the dilute acids, and is the basis of the ordinary manganesian salts, which are soluble in water, and are nearly colorless when pure, but often have a slightly pink hue. When ammonia is added to solutions of this oxide, the whole is not precipitated, but a double salt is formed, as with magnesia: thus $2[MnO,SO_3]+NH_3=[MnO,NH_32SO_3]+MnO$. When the salts of this oxide are decomposed by potassa or soda, a bulky white precipitate falls, which is *hydrated protoxide* of manganese; it speedily becomes brown by exposure to air, absorbing oxygen and a little carbonic acid; and, when collected and washed upon a filter, it gradually becomes a hydrate of the sesquioxide. A similar change is immediately produced by solution of chlorine or chloride of lime, by which a hydrate of the sesquioxide, or of the binoxide is formed. The recently precipitated and moist hydrate of the protoxide is soluble in ammonia, but not in potassa or soda.

SESQUIOXIDE OF MANGANESE; MANGANIC OXIDE; (Mn_2O_3).—When protoxide or carbonate of manganese is exposed for some time to a red heat in an open vessel, it absorbs oxygen, and is converted into a deep-brown powder. An oxide similarly constituted is also obtained by heating the pure peroxide in a platinum crucible till it ceases to give out oxygen at dull redness. By exposing protonitrate of manganese to a red heat, the sesquioxide remains as a black powder; and this is the most certain way of obtaining it. The characters of this oxide, in respect to solvents, differ with its state of aggregation; its acid solutions which are at first red, become colorless when heated, when exposed to air and light, or in contact with organic matter, and deposit peroxide, while a portion of protoxide remains in solution. They are rendered colorless by sulphuretted hydrogen, by sulphurous acid, and some other deoxidizers. Heated with hydrochloric acid, it evolves chlorine; and with sulphuric acid, oxygen; and a protochloride and protosulphate of manganese result. Digested with nitric acid, protonitrate and peroxide are formed. As a base, this oxide is isomorphous with sesquioxide of iron (Fe_2O_3), and with alumina (Al_2O_3). It gives a violet, or, in small quantity, a pink tinge, to glass, and appears to be the coloring principle of amethyst. It constitutes the mineral called *braunite*, which occurs in octahedral crystals.

Hydrated Sesquioxide of Manganese (Mn_2O_3+HO) is obtained by exposing the hydrated and moist protoxide to the action of air; or by passing chlorine through water holding protocarbonate of manganese in suspension, and leaving excess of the latter; for if the chlorine be in excess, hydrated binoxide is formed. It is a common natural product (the *manganite* of mineralogists), occurring crystallized and massive, sp. gr. 4·3, and so closely resembling the peroxide, that it is often difficult to distinguish them; the powder of the hydrated sesquioxide is, however, generally *brown*, that of the peroxide *black;* the former, heated in a tube, gives off water and little oxygen; the latter little moisture and much oxygen.

BINOXIDE OF MANGANESE; PEROXIDE OF MANGANESE (MnO_2).—This is the oxide which most frequently occurs *native.* It is common in Devonshire, Somersetshire, and Aberdeenshire. It is found in a variety of forms: compact and massive, pulverulent and crystallized. Many of the latter varieties have a gray metallic lustre, and are found acicularly radiated, and in rhomboidal prisms. Its specific gravity varies between 4·8 and 4·9. It is the *pyrolusite* of some mineralogists. Under the name of *manganese* it is met with in commerce, and is largely consumed in the manufacture of bleaching compounds. In the laboratory, it is resorted to as a source of oxygen gas, ($2MnO_2=Mn_2O_3+O$,) for which purpose it should be well dried before it is heated. Carbonate of lime, silica, oxide of iron, and some other substances, are not unfrequently associated with it. In the arts it is used to give a black color to earthenware, and to remove the green color which glass derives from protoxide of iron; in this case MnO_2, acting on $2FeO$, produces MnO and Fe_2O_3. A little excess of oxide of manganese is apt to give the pink tint, which is sometimes seen in plate-glass windows. This oxide is a good conductor of electricity. It forms no combinations with the acids; but such of them as appear to dissolve it, reduce it to the state of protoxide. Gently heated with hydrochloric acid, chlorine is liberated, in consequence of the decomposition of the acid by the oxygen of the oxide ($MnO_2+2HCl=MnCl+2HO+Cl$.) The chloride in solution has all the properties of the protosalts of manganese. Boiled with sulphuric acid, oxygen is evolved, and a soluble sulphate of the protoxide is formed, [$MnO_2,+SO_3=MnO,SO_3+O$]. Nitric acid does not attack it unless it contains sesquioxide, or some deoxidizing agent is at the same time present. Many vegetable acids decompose it by the aid of heat.

The commercial value of this oxide may be said to depend upon the proportion of chlorine which a given weight of it will evolve when heated with hydrochloric acid; or, in other words, the quantity of oxygen which it contains beyond that contained in the protoxide. The usual mode of determining this excess of oxygen, is founded upon the mutual action of the oxide and oxalic acid in the presence of free sulphuric acid, when protosulphate of manganese and carbonic acid are formed.

A hydrated peroxide, $=MnO_2,+HO$, is formed by precipitating protochloride of manganese by chloride of lime. In this state it is brown, while the anhydrous oxide is black. The soft black mineral known under the name of *Wad*, is also a hydrate of this peroxide.

RED OXIDE OF MANGANESE (Mn_3O_4).—This oxide exists native, constituting the mineral termed *Hausmannite.* It is said to be formed when the hydrated protocarbonate of manganese, after having been dried, is exposed in the air to a red heat.

VARVICITE (Mn_4O_7).—This name has been given to a peculiar oxide of manganese from Warwickshire. It is harder and has more lustre than the native peroxide.

MANGANIC ACID (MnO_3).—This acid is met with only in a state of combination with alkaline bases. It may be obtained as manganate of potassa by fusing equal parts of peroxide of manganese in fine powder, and hydrate of potassa, with a small quantity of nitrate, in a covered crucible; a greenish-black mass results, which with water affords a deep green solution of manganate of potassa. This is permanent with excess of alkali, but otherwise it becomes blue, purple, and ultimately red on exposure to air, in consequence of the formation of permanganate of potassa by the absorption of oxygen (*chameleon mineral*). At the same time it deposits a brown powder, which is hydrated peroxide of manganese, and free alkali is separated: ($3[KO, MnO_3] = KO,Mn_2O_7 + MnO_2 + 2KO$.) Nitric acid, added to the liquid, changes the green into the red compound. When set free from the base, manganic acid is resolved into hydrated peroxide and oxygen.

Manganate of Potassa (KO,MnO_3), may be obtained in a purer state as follows: Mix 4 parts of finely-powdered peroxide of manganese with 3½ of chlorate of potassa, and add them to 5 parts of hydrate of potassa dissolved in a small quantity of water. The mixture is evaporated to dryness powdered, and then ignited in a platinum crucible, but not fused, at a low red heat. Digested in a small quantity of cold water, and filtered through asbestos, this affords a deep emerald green solution of the alkaline manganate, which may be obtained in crystals of the same color by evaporating the solution over sulphuric acid in the air-pump. The crystals are isomorphous with the sulphate and chromate of potassa. They are anhydrous. They are soluble in a moderately concentrated solution of potassa, forming an intensely green solution, and are again deposited without change when evaporated in vacuo. The changes of color which the compound undergoes may be well illustrated by placing a quantity of the manganate in powder in a capacious jar, and very gradually adding to it a large quantity of water which is aërated. As the oxygen is absorbed by the manganic action, it changes in color from emerald green to blue, violet, purple, and at length remains of a ruby or amethyst red. It is now permanganate of potassa. This conversion is immediately brought about by the addition of an acid, even by acetic acid. Acids operate by removing the base. The change is also rapidly effected by boiling, showing that the manganic is a very unstable acid. It is reduced to the state of hydrated peroxide by organic matter. It is instantly decomposed and rendered colorless by sulphurous, phosphorous, and nitrous acids. Arsenious acid also reduces it. The tendency of this acid therefore is to pass either to a lower or higher state of oxidation.

PERMANGANIC ACID (Mn_2O_7).—When the green solution of manganate of potassa in water, moderately diluted, is boiled, it rapidly becomes purple by conversion into the permanganate of potassa (KO,Mn_2O_7). As the solution is decomposed by organic matter, it must be filtered through asbestos, and concentrated by evaporation. Deep ruby-colored crystals are thus obtained, which are soluble in 16 parts of water at 60°, and possess an intense coloring power; one or two grains will give a deep amethyst red tint to a large quantity of water.

The solution of this salt is now much employed in volumetric analysis. It readily parts with its oxygen to organic matter and deoxidizing bodies generally; it loses its color, and brown hydrated peroxide of manganese is deposited. Thus the color of the permanganate is discharged by sulphurous, phosphorous, nitrous, and arsenious acids, as well as by their salts when an acid is added. Sulphuretted hydrogen, a protosalt of iron (p. 369), grape-sugar, and nicotina immediately deoxidize it. Iodide of potassium converts a concentrated solution to green manganate, but deoxidizes entirely a weak solution. A standard solution of the permanganate has been employed for determining the amount of organic matter in air and water (pp. 120 and 151). Under the name of *Condy's Disinfecting Liquid*, it has been much used for the removal of foul effluvia in sick rooms. A solution of it is sold under the name of *ozonized water*.

If a solution of nitrate of silver is added to a hot concentrated solution of permanganate of potassa, red crystals of permanganate of silver are deposited on cooling. By double decomposition with the chlorides, permanganates of the alkaline earths may be obtained. If a concentrated solution of potassa is poured into a diluted solution of permanganate, the liquid becomes first violet and by very gradual additions of the alkali, passes through various shades of purple to emerald green. Manganate of potassa is formed, and a double quantity of base enters into combination ($KO,Mn_2O_7+KO=2(KO,MnO_3)+O$): the oxygen being retained in the liquid. A permanganate is more stable in water than a manganate, since it may be boiled without being decomposed. The acid is, however, slowly changed by exposure to air, into peroxide of manganese.

Permanganic acid may be obtained in combination with water, by decomposing permanganate of baryta with diluted sulphuric acid. Its formula is HO,Mn_2O_7. The solution is of a red color. It is rapidly decomposed even at common temperatures. A portion of the oxygen in this acid is supposed by Schönbein to be in an allotropic state, as ozone (p. 103).

PROTOCHLORIDE OF MANGANESE ($MnCl$).—When peroxide of manganese is heated with hydrochlorate of ammonia, a solution of *chloride of manganese* may be obtained from the residue, which furnishes transparent pinkish crystals of hydrated chloride. The same salt is obtained by dissolving carbonate of manganese in dilute hydrochloric acid, and evaporating the solution. The higher oxides of this metal, when treated with hydrochloric acid, give off chlorine, and are converted into protochloride of manganese. Thus a manganate, treated with an excess of hydrochloric acid, acquires the usual chemical properties of the protosalts.

A large quantity of this chloride, in an impure state, is obtained as a waste product in the manufacture of chloride of lime.

Exposed, out of the contact of air, to a red heat, the hydrated crystals of this protochloride lose water to the amount of about 40 per cent., and leave a lamellar anhydrous chloride of manganese; heated in the contact of air, this chloride is decomposed and converted into an oxide, as is the case with the corresponding chloride of magnesium. 100 parts of water at 60° dissolve about 40 parts of the anhydrous salt: alcohol dissolves half its weight, and the solution, when evaporated *in vacuo*, affords a crystalline *alcoate*, containing two equivalents of alcohol.

When ammonia is added to a solution of the chloride, half of the manganese is thrown down in the state of hydrated protoxide, and the remainder forms a double salt. When a recently precipitated hydrated protoxide of manganese is digested in a solution of sal-ammoniac, the double chloride is formed.

SESQUICHLORIDE OF MANGANESE (Mn_2Cl_3) is formed when the sesquioxide is dissolved at a low temperature in hydrochloric acid; a dark brown solution is obtained which, by a slight elevation of temperature, evolves chlorine.

PERCHLORIDE OF MANGANESE (Mn_2Cl_7) is produced by adding fused chloride of sodium to a solution of permanganate of potassa in sulphuric acid; the compound passes off in the form of a green vapor, condensible at 0° into an olive-colored liquid. If the vapor be conveyed into a moistened flask, it acquires a red tint, and hydrochloric and permanganic acids are generated.

NITRATE OF MANGANESE (MnO,NO_5).—Dilute nitric acid dissolves moist protoxide or protocarbonate of manganese, and forms a *protonitrate*, which may be obtained by evaporation *in vacuo*, in hydrated prismatic crystals, deliquescent, very soluble in water and in alcohol, and of a bitter taste; their alcoholic solution burns with a green flame.

SULPHIDE OF MANGANESE (MnS).—When dried protosulphate of manganese is ignited with one-sixth its weight of finely-powdered charcoal, or when a current of sulphuretted hydrogen is passed over the protocarbonate or protosulphate heated to redness, a *sulphide of manganese* is obtained. It has a gray metallic lustre, and is soluble in dilute sulphuric and hydrochloric acid, with the evolution of sulphuretted hydrogen. It is identical with the *native sulphide of manganese*, a rare ore, found in Cornwall and Transylvania.

SULPHATE OF MANGANESE (MnO,SO_3) is formed by dissolving the protoxide or protocarbonate in dilute sulphuric acid, or by mixing peroxide of manganese into a paste with sulphuric acid, and heating the mixture to dull redness; oxygen is evolved, and the dry mass washed with water affords a solution of the sulphate of the protoxide, which may be crystallized by evaporation. This salt is used in dyeing and calico-printing. When cloth is passed through its solution, and afterwards through a caustic alkali, protoxide of manganese is precipitated upon it and rapidly becomes brown in the air; or it is at once peroxidized by passing the cloth through a solution of chloride of lime. This color is called *manganese brown.*

Sulphate of manganese, as it is obtained by gentle evaporation from the neutral solution, forms rhombic prisms which contain 4 atoms of water. When the crystals are formed between 45° and 68° they contain 5 atoms of water; when formed under 42° they include 7 atoms of water; and when a concentrated solution of sulphate of manganese is mixed with sulphuric acid, it yields on evaporation small granular crystals containing only 1 atom of water. The solubility of sulphate of manganese varies with its water of crystallization; the anhydrous salt is soluble in 2 parts of water at 60°, and in its own weight at 212°. It is insoluble in alcohol. The taste of sulphate of manganese is styptic and bitterish, and the crystals have generally a slight tinge of pink. At 240°, they lose 3 atoms of water, but retain 1 until heated above 400°; at a red heat the salt becomes anhydrous. This compound forms double salts with potassa and ammonia.

SESQUISULPHATE OF MANGANESE ($Mn_2O_3+3SO_3$) is formed by dissolving the sesquioxide in sulphuric acid: the solution is of a crimson color. When heated it gives off oxygen and becomes colorless: it is instantly bleached by sulphurous acid or any deoxidizing agent. Its most important property is that of forming, with sulphate of potassa or of ammonia, double salts crystallizing in octahedra, which are *manganese alums*, similar in constitution to ordinary alum, but with Al_2O_3, replaced by Mn_2O_3 (p. 342). 1 part of peroxide of manganese mixed with 13 of oil of vitriol, and gently heated till half the quantity of oxygen thus separable has escaped, yields a mass from which water extracts the sesquisulphate; 1 part gives a red color to 1280 parts of water.

CARBIDE OF MANGANESE is probably always contained in the metal reduced by charcoal. The quality of steel is said to be improved by the presence in it of carbide of manganese. The plumbago-like substance called *kish*, occasionally produced in iron furnaces, contains this carbide.

CARBONATE OF MANGANESE (MnO,CO_2) is white, insipid, and insoluble in water. It is precipitated as a hydrate, by alkaline carbonates, from the protochloride or protosulphate: it becomes brown by drying in the air. Carbonate of manganese constitutes the *spathose* manganese of mineralogy, and often accompanies spathose iron.

TESTS FOR THE SALTS OF MANGANESE.—The proto-salts are soluble in water. The solution is either colorless or slightly pink, and has an acid reaction. It has a bitter astringent taste, and becomes brown and turbid when long exposed. 1. *Sulphuretted hydrogen* produces no precipitate, but hydrosulphate of ammonia throws down a flesh-colored sulphide, which is easily dissolved by acetic acid. The precipitate becomes brown by exposure to air. 2. *Potassa* or *soda* throws down a white hydrated oxide, which rapidly becomes brown on exposure, owing to its conversion into sesquioxide. Before undergoing this change the precipitate is soluble in hydrochlorate of ammonia: it is insoluble in potassa or soda. 3. Ammonia also precipitates partially a white hydrated oxide, which becomes brown when exposed. 4. *Carbonates* and *bicarbonates* of potassa, soda, or ammonia, throw down a white carbonate, which is dissolved by hydrochlorate of ammonia, and becomes *slowly* brown by exposure. 5. Ferrocyanide of potassium produces a white precipitate, with a shade of blue if iron is present, and red if copper is present. 6. Ferricyanide of potassium gives a brownish-red precipitate. 7. Chlorine produces no effect on the solution, but when any alkali is added, brown hydrated peroxide of manganese is precipitated. Chloride of lime immediately gives a brown precipitate. 8. Heat a few grains of minium in a few drops of strong nitric acid, and add to the liquid a small quantity of the peroxide of manganese. Permanganic acid is produced, which may be recognized by the pink color of the solution, so soon as the oxide of lead has subsided. 9. On a loop of platinum wire melt some carbonate of soda with a little nitre. If a mere trace of oxide of manganese be fused with the mixed salts in the inner flame of the blowpipe, or of a Bunsen's jet, manganate of soda is produced, known by its greenish color (if the manganese is not in excess). If the wire is placed in a few drops of water in a tube, an emerald green solution is obtained, which, when diluted and warmed, or an acid is added, is converted into a pink solution of permanganate of potassa. This is probably the most delicate test for manganese, whether in soluble or in an insoluble form.

CHAPTER XXXI.

ZINC—TIN—CADMIUM.

ZINC ($Zn=32$).

THE Zinc of commerce is procured from the native sulphide or carbonate (*calamine*). The ore is picked, broken into small pieces, submitted to a dull red heat in a reverberatory furnace, by which carbonic acid is driven off from the calamine, and sulphur from the sulphide. It is then washed, ground, and thoroughly mixed with about one-eighth of its weight of powdered charcoal. This mixture is put into large earthen pots, not unlike oil-jars, six of which are usually placed in a circular furnace. Each pot has an iron tube passing form its lower part, through the floor of the furnace, and dipping into water; they are everywhere else firmly luted. Upon the application of a full red heat, the metal distils through the tube into the water beneath, whence it is collected, melted, and cast into cakes. This process is called *distillatio per descensum*. Commercial zinc generally contains traces of sulphur, iron, and arsenic.

Zinc is a bluish-white metal, with considerable lustre, rather hard, of a specific gravity of about 6·8 in its usual state, but when drawn into wire, or rolled into plates, its density is augmented to 7· or 7·1. It has a peculiar odor when breathed upon, or handled with moist fingers. In its ordinary state and at common temperatures it is tough, but becomes brittle when its temperature approaches that of fusion, which is about 770°. At a temperature a little above 212°, and between that and 300°, it is ductile and malleable, and may be rolled into thin leaves or drawn into wire. If slowly cooled after fusion, its fracture is very crystalline. It is volatile at a bright red heat, and admits of distillation, but if its vapor be exposed to air, it burns with intense brilliancy.

When a surface of clean and polished zinc is exposed to dry air, it remains bright; in damp air it tarnishes, and then remains unchanged. Under water it becomes enfilmed with hydrated oxide, or with a hydrated basic carbonate if carbonic acid be present. At common temperatures it does not decompose water, but does so at a red heat, or in the presence of acids. In pure water, from which air has been carefully excluded, it remains bright. The energy with which zinc is acted on by dilute sulphuric acid is greatly dependent upon the purity of the metal; when perfectly pure the action is feeble, but when it contains minute portions of other metals, it becomes rapid: this is apparently owing to a galvanic action; and when a piece of pure zinc is wound round with platinum wire an equivalent effect is produced. Zinc and all its compounds, excepting blende, are soluble in hydrochloric acid; hydrogen is evolved, when the metal is employed. A strong solution of potassa, or soda, when heated, also dissolves the metal with the evolution of hydrogen. If the zinc contains arsenic, the hydrogen evolved, whether as the result of the action of an acid or an alkali, is mixed with arsenuretted hydrogen. This may be inferred when the gas blackens paper impregnated with a solution of nitrate of silver. Phosphorus combined with hydrogen will produce a similar action on nitrate of silver. If the hydrogen contains sulphur, this will be indicated by the discoloration of paper impregnated with a salt of lead. Zinc, in consequence of its lightness and cheapness, is much used for roofing, gutters, and chimney-tops; but it should not, as is sometimes the case, be riveted with copper or iron nails, the contact of which with the zinc accelerates the destruction of the latter by electric action; indeed, any of the common metals in metallic contact with zinc, tend to produce its oxidation.

ZINC AND OXYGEN.—The high attraction between zinc and oxygen is shown by the facility with which many of the other metallic oxides, in solution, are reduced to the metallic state by its means. Its important electrogenerative power in Voltaic arrangements, is also referable to this cause. By exposing zinc to the joint action of heat and air, at a temperature just sufficient to fuse it, it is converted into a gray powder, which is probably a mere mixture of metallic zinc and oxide of zinc, although by some it is regarded as a true *suboxide*, Zn_2O.

Oxide of Zinc (ZnO).—This is the only salifiable oxide of zinc; it is obtained by intensely heating the metal exposed to air, when its vapor takes fire, burns with a very bright flame, and forms a white flocculent substance, formerly called *nihil album*, *philosopher's wool*, and *flowers of zinc*. When this combustion goes on with violence, the oxide, though in itself not volatile, is carried up in flocculi by the current of air, which are so light as to remain for a long time floating about the atmosphere. A piece of zinc-leaf may also be inflamed by a spirit-lamp, and will continue to burn brilliantly even when removed from the flame; if inflamed and plunged into oxygen, the combustion is as vivid as that of phosphorus—indeed, the splendor of the flame probably arises in both instances from the same cause, namely, the ignition of finely-divided solid incombustible matter (p. 97). The oxide of zinc, as prepared by combustion, generally contains small particles of the metal, which render it gritty: it may also contain other impurities, so that for pharmaceutical use it should be procured by decomposing a solution of pure sulphate of zinc at a boiling heat by its equivalent of carbonate of soda. The precipitate well washed, dried, and exposed to a dull-red heat, is a pure oxide: or the cold solution of the sulphate may be decomposed by carbonate of ammonia, and the precipitate washed and dried as before. Traces of sulphuric acid, or of soda, may be detected in the oxide from cold solutions when carbonate of soda has been used, and if a hot solution be precipitated by carbonate of ammonia, the oxide will retain sulphuric acid.

Oxide of zinc obtained by the combustion of the metal, or by passing steam over red-hot zinc, is sometimes crystalline; its specific gravity is between 5·6 and 5·7. It is commonly met with in the form of a white powder, which at a high temperature acquires a yellow tint, but again whitens as it cools. It has been used as a pigment, both with oil and water; and is employed in medicine as a tonic, and as an external application. Oxide of zinc is readily soluble in acids; it also dissolves, especially in the state of hydrate, in the caustic fixed alkalies, and in pure and carbonated ammonia. The strong ammoniacal solution becomes turbid when dilute, and deposits the oxide when boiled. When a solution of alumina in caustic potassa is mixed with an ammoniacal solution of oxide of zinc, a definite combination of the two oxides is thrown down, containing 6 atoms of alumina and 1 of oxide of zinc, being identical in composition with the mineral called *Gahnite*.

Nitrate of Zinc ($ZnO,NO_5,6HO$) is a deliquescent salt, which crystallizes with difficulty in four-sided prisms: it is very soluble in water and in alcohol.

Chloride of Zinc ($ZnCl$) is formed by heating leaf-zinc in chlorine; or by evaporating a solution of zinc in hydrochloric acid to dryness, and heating the residue to dull redness. It is a white translucent substance, extremely deliquescent, fusible at 300°, and volatile at a bright-red heat: its vapor condenses in acicular crystals. It has a nauseous styptic taste, and is powerfully emetic. It was formerly called *butter of zinc*. It is readily soluble in water, and the solution gives on evaporation a difficultly crystallizable and deliquescent hydrate ($ZnCl,HO$), which, when heated in the open air, partly sublimes in the form of chloride, and is partly resolved into hydrochloric acid and oxide of zinc. Sir William Burnett's disinfectant liquid, and preservative against dry-rot, is a strong solution of chloride of zinc; its sp. gr. is 1·019. Chloride of zinc forms several double salts, with the chlorides of the alkaline metals. Zinc combines directly with bromine and iodine to form a *bromide* and an *iodide*.

Sulphide of Zinc (ZnS) may be formed by heating oxide of zinc with excess of sulphur; it is also produced by heating a mixture of zinc filings and sulphide of mercury. When a salt of zinc is precipitated by an alkaline sulphide, a white compound is obtained, which is probably a monohydrated sulphide of zinc. *Native Sulphide of Zinc*, or *Blende*, occurs in crystals which are brittle, soft, and of different shades of brown and black. Its primitive form is the rhomboidal dodecahedron. It usually contains traces of iron and lead. It is an abundant mineral, and important as a source of the metal, which is obtained by roasting the ore, and afterwards exposing it to heat in proper distillatory vessels, mixed with charcoal. The English miners call it *black jack*. It is dissolved by nitrohydrochloric acid.

SULPHATE OF ZINC (ZnO,SO_3).—Zinc is readily oxidized and dissolved by dilute sulphuric acid, and hydrogen is given off; the zinc so decomposes water that an atom of zinc is substituted for an atom of hydrogen: $HO,SO_3+Zn=ZnO,SO_3+H$; and a solution of *sulphate of zinc* results, which by evaporation affords crystals$=ZnO,SO_3,7HO$, in the form of right rhombic prisms. This salt is soluble at 2·5 parts of water at 60°. The crystals are slightly efflorescent: at 212° they lose 6 atoms of water, retaining 1 till heated nearly to dull redness. The *anhydrous sulphate* is white and friable; exposed to humid air it gradually resumes 7 atoms of water; it heats when sprinkled with water; at a high temperature it evolves sulphuric and sulphurous acid and oxygen, and at a white heat is decomposed, leaving oxide of zinc. It is soluble in hydrochloric acid without decomposition. *White vitriol*, or the sulphate of zinc of commerce, is often obtained by the oxidation of blende, and is impure; it generally contains a sulphate of zinc, together with the sulphates of iron, copper, cadmium, alumina, and sometimes lead: it usually occurs in amorphous masses. The sulphate, like the chloride of zinc, forms double salts with the sulphates of the alkalies.

CARBONATE OF ZINC.—The precipitate formed by adding carbonate of potassa to sulphate of zinc is a mixture of carbonate and hydrated oxide, analogous to the *magnesia alba*, its formula being $2(ZnO,CO_2)+3(ZnO,HO,)$ or when precipitated in the cold, $ZnO,CO_2+2(ZnO,HO)$.

Native Carbonate of Zinc or *Calamine*, occurs both crystallized and massive. It is often found investing carbonate of lime, which has sometimes been decomposed, and the calamine remains in pseudo-crystals. It abounds in Somersetshire, Flintshire, and Derbyshire. A beautiful variety colored by carbonate of copper is found at Matlock. The variety of calamine known by the name of *electric calamine*, from its property of becoming electrical when gently heated, consists of oxide of zinc in combination with silica.

Zinced Iron; Galvanized Iron.—If plates of hot iron be dipped into melted zinc, they acquire the appearance of tin-plate, for which they are a valuable substitute, inasmuch as the zinced iron is prevented from oxidation and rusting, by the electrical relations of the metals; the zinc, it is true, is more subject to oxidation than tin, but so long as any of it remains, the iron is protected, and when covered by a coat of paint is extremely durable. Hurdles, fences, and all out of door iron-work, as well as implements used in damp situations, and employed in contact with water, may be thus defended. The wires of electric telegraphs are generally of zinced iron, and their section, when exposed to air and water, sometimes exhibits a fresh deposition of zinc, arising from the galvanic precipitation of small portions of dissolved zinc upon the electro-negative iron. The zincing of iron is generally performed by dipping the iron, previously well cleaned, into melted zinc, the surface of which is kept carefully covered with sal-ammoniac to prevent oxidation, and so enable the iron to become thoroughly wetted as it were, and superficially combined with the zinc. The zinc is fused in large wrought iron vessels, placed over proper furnaces, and after the frequent dippings of the iron articles, there is ultimately found at the bottom of the melted metal, a quantity of a granular alloy of zinc and iron. The process is not applicable to the generality of vessels used for culinary purposes, in consequence of the contaminations by oxide of zinc which would often ensue, especially with acidulous liquors. In using zinced iron, care should be taken that where nails or rivets are required, they should also be coated with zinc.

TESTS FOR THE SALTS OF ZINC.—They are mostly soluble in water; the solutions are colorless, and have an astringent and metallic taste. 1. *Potassa, soda,* and *ammonia,* form white precipitates, soluble in an excess of the alkali, and in dilute sulphuric acid. In this case the precipitate is distinguished from alumina by its solubility in excess of ammonia, as well as in chloride of ammonium. 2. The precipitate formed in solutions of zinc by the *carbonates of potassa and soda* is not soluble in excess of these carbonates, but when *carbonate of ammonia* is employed, the precipitate produced is again dissolved. Zinc is thus separated from alumina and alkaline earths. 3. *Sulphuretted hydrogen* throws down a white hydrated sulphide of zinc in neutral solutions, but not in those which are acid or alkaline. 4. Hydrosulphate of ammonia produces a white, or yellowish-white precipitate. 5. *Ferrocyanide of potassium* gives a white bulky precipitate, and ferricyanide a brownish precipitate. The soluble phosphates, oxalates, and borates, produce white precipitates soluble in acids and alkalies. The salts of zinc which are insoluble in water, dissolve in dilute sulphuric acid, and are precipitated by ammonia, but are redissolved by an excess of acid or of precipitant. Metallic zinc is not thrown down from its solutions by the other metals, with the occasional exception, however, of iron.

The special characters of a salt of zinc are, that the oxide is soluble both in potassa and ammonia, and that from the alkaline solutions it is precipitated as a white sulphide by sulphuretted hydrogen, but it is not precipitated from them by chloride of ammonium. By these characters it is distinguished from alumina and other oxides which are soluble in potassa. Zinc is the only metal which forms a white sulphide with sulphuretted hydrogen.

Before the blowpipe, or on platinum foil, *oxide of zinc* becomes yellow when heated, but whitens as it cools. A small proportion forms with borax a clear glass, which becomes opaque on increasing the quantity of oxide. If a drop of nitrate of cobalt is added to the oxide, and this is dried and ignited, it becomes green. With soda, in the interior flame, oxide of zinc is reduced, and the metal burns with its characteristic flame, depositing its oxide upon the charcoal. Mixed with oxide of copper, and reduced, the zinc will be fixed and brass obtained.

TIN ($Sn=50$).

TIN (Jupiter ♃ of the alchemists) has been known from remote ages, and was obtained at a very early period from Spain and Britain by the Phœnicians. It occurs most abundantly in Cornwall, the mines of which afford about 3000 tons annually: it is also found in Germany, Bohemia and Hungary; in Chili and Mexico; in the Peninsula of Malacca; and in India, in the Island of Banca. The *native peroxide* is the principal *ore of tin:* the metal is obtained by heating it to redness with charcoal or culm, and a little lime; the first product is impure and is returned into the furnace, and carefully heated so as to fuse the tin, which runs off into an iron kettle, while the principal impurities remain unmelted; in the kettle the tin is kept in fusion, stirred, and agitated by plunging wet charcoal into it, by which a quantity of impurities collect upon the surface, and are removed by a skimmer: thus refined, the metal is cast into blocks of about 3 cwt. each. The common ores are known under the name of *mine tin,* and furnish a less pure metal than that obtained from *stream tin.* The purest tin is known under the name of *grain tin,* a term formerly applied exclusively to the metal obtained from the stream ore: *block tin* is less pure, and is the produce of the common ore. The peculiar columnar fracture which pure tin exhibits when broken, is given by heating the ingot till it becomes brittle, and then letting it fall from a height upon a hard pavement.

Tin has a silvery-white color, with a slight tint of yellow, and when so viewed as to exclude the white light reflected from its surface, it is decidedly yellow: it is softer than gold, but harder than lead: it is malleable, though imperfectly ductile. What is termed *tin-foil* is the metal beaten out into thin leaves, but it is seldom pure: the common commercial article generally contains from 30 to 40 per cent. of lead; and the foil frequently used for packing articles of food, confectionery, tea, &c., is lead thinly plated with tin, and is more easily oxidized than the separate metals, so that it may in some cases give rise to lead-poisoning. Traces of arsenic are also not uncommon in it. The sp. gr. of tin fluctuates from 7·28 to 7·6, the lightest being the purest metal. When bent, it occasions a peculiar crackling noise; and when rapidly bent backwards and forwards several times successively, it becomes hot. When rubbed, it exhales a peculiar odor. It melts at 442°, and slightly contracts on consolidation. By exposure to heat and air it is gradually converted into protoxide; but if the heat be continued till metallic tin no longer remains, the protoxide passes into peroxide. Placed upon ignited charcoal under a current of oxygen gas, it enters into rapid combustion, forming the peroxide; and if an intensely-heated globule of the metal be thrown upon a sheet of dark-colored paper, it subdivides into small particles, which burn very brilliantly, and leave lines of white oxide. It volatilizes at a very high temperature. When a polished surface of tin is heated it becomes yellow and iridescent, in consequence of superficial oxidation. A preparation, under the name of *powdered tin*, is sometimes made by shaking the melted metal in a wooden box rubbed with chalk on the inside. The substance called *tin putty*, used for polishing plate, is made by levigating the crusts of oxide that form on melted tin.

PROTOXIDE OF TIN; STANNOUS OXIDE (SnO) is obtained by precipitating a solution of protochloride of tin by ammonia; it falls in the state of *hydrate:* when dried, out of the contact of air, it is of a dark color. When the protochloride is decomposed by a carbonated alkali, the precipitate is also a *hydrated protoxide*, retaining no carbonic acid. It is obtained *anhydrous*, by heating it in a glass tube, passing a current of dry carbonic acid over it till the water is carried off, and suffering it to cool out of the contact of air. The specific gravity of this oxide is 6·6. It forms a dark-gray or black powder, which, on the contact of a red-hot wire, burns like tinder into peroxide. In the hydrated state it dissolves readily in sulphuric, hydrochloric, and dilute nitric acids, as well as in caustic potassa and soda, but not in ammonia, nor in the alkaline carbonates. It is soluble in lime-water, and in baryta-water. Its alkaline solution, when long kept, deposits metallic tin in arborescent crystals, and becomes a solution of the peroxide.

SESQUIOXIDE OF TIN (Sn_2O_3).—When a solution of protochloride of tin is mixed with moist hydrated sesquioxide of iron and boiled, an interchange of elements takes place, by which protochloride of iron and sesquioxide of tin are formed: in this case, $2(SnCl)$ and Fe_2O_3, become Sn_2O_3 and $2(FeCl)$. The solubility of this oxide in ammonia distinguishes it from protoxide; and its giving a purple precipitate with chloride of gold from peroxide. It is soluble in concentrated hydrochloric acid. It may be represented as a stannate of the protoxide by the formula SnO,SnO_2.

PEROXIDE OF TIN; BINOXIDE OF TIN (SnO_2).—This is the common ore of tin: in its crystalline form it is insoluble in acids, but when heated with potassa or soda it forms a soluble compound. There are two remarkable varieties of the hydrate of this oxide, which have been distinguished as *stannic* and *metastannic acid*. *Stannic acid* (SnO_2HO) is obtained by precipitating a solution of bichloride of tin by ammonia, and washing and carefully drying the precipitate: it is soluble in acids, and in solutions of potassa and soda, but not in ammonia. When heated to about 300°, it passes into metastannic acid. *Stannate of potassa* is formed when peroxide of tin is heated with potassa: the product, when dissolved and evaporated, yields crystals ($KO,SnO_2,4HO$). Their aqueous solution is alkaline, absorbs carbonic acid, and is precipitated by most of the salts of potassa, soda, and ammonia. *Stannate of soda* ($NaO,SnO_2,4HO$) may be similarly prepared and crystallized: it is largely used as a mordant by dyers and calico-printers.

Metastannic acid is the result of the action of nitric acid upon tin: in its most concentrated form this acid does not immediately act, but on the addition of a few drops of water violent effervescence ensues, much heat is evolved, together with nitric oxide and nitrous acid vapor; some nitrate of ammonia is also formed (p. 168); and the metastannic acid remains in the form of a white insoluble powder: it may be purified by washing, and dried at a dull-red heat. When dried in the air it consists of $Sn_5O_{10},10HO$: dried at 212° it loses 5HO, and at a red heat becomes anhydrous, and acquires a pale buff color. Hydrated metastannic acid is insoluble in nitric acid: it dissolves in sulphuric acid, forming a compound soluble in water, but decomposed by boiling. It dissolves in solutions of potassa and soda and their carbonates, but not in ammonia. The *metastannates* are not crystallizable. When the hydrated acid is moistened with protochloride of tin it forms a characteristic yellow *metastannate of tin*.

Native Peroxide of Tin is generally gray, brown, or black, and sometimes transparent or translucent; its specific gravity is 7: its primitive crystal is an obtuse octahedron, of which the modifications are extremely numerous. In some of the valleys of Cornwall it is found in nodules mixed with pebbles, and is called *stream tin*. A modification of stream tin, in small banded fragments or globular masses, is called *wood tin*.

PROTOCHLORIDE OF TIN ($SnCl$) is obtained by subjecting a mixture of equal weights of calomel and of an amalgam of tin and mercury to distillation, in a retort gradually raised to a dull-red heat; or a mixture of 1 part of tin filings and 2 of corrosive sublimate may be treated in the same way. When hydrochloric acid gas is passed over heated tin a glass tube, the protochloride is also formed and hydrogen given off. When tin is dissolved in hydrochloric acid, the solution evaporated, and the dry residue carefully heated to incipient redness in a small tube retort, so as to exclude air, the protochloride of tin remains nearly pure. It is in the form of a gray solid, fusible and volatile at a high heat (*Butter of Tin*). When its solution in a small quantity of water is evaporated it yields prismatic crystals, which include 3 atoms of water, of which the greater part may be expelled at 212°. When a large quantity of water is poured upon these crystals they are partly decomposed, hydrochloric acid is separated, and a white powder formed, which is an *oxichloride of tin*$=SnO,SnCl,2HO$. The protochloride of tin, or *salt of tin* of commerce, is made by putting 1 part of granulated tin into a basin upon a sand-bath, and pouring upon it 1 part of hydrochloric acid, so that when heated it may be exposed to the joint action of the acid and air; after some hours 3 parts more of the acid are added, and the mixture stirred and digested till a saturated solution is obtained. During the process, fetid hydrogen gas is given off, and the greater part of the tin is dissolved; when the clear liquor is poured off it is set aside to crystallize; the mother-liquors are again evaporated as long as they afford crystals, and the residue is afterwards employed for conversion into bichloride.

In consequence of the decomposition above mentioned, the aqueous solution of protochloride of tin is turbid, but becomes clear on the addition of hydrochloric acid. This acid solution quickly absorbs oxygen, and, when added to certain metallic solutions, it revives or deoxidizes them. It precipitates sulphur from sulphurous acid. It reduces the persalts of iron to protosalts, and converts arsenic acid into arsenious acid, and chromic acid into oxide of chromium. With a weak solution of corrosive sublimate it forms a gray precipitate of metallic mercury. Added to a dilute solution of chloride of platinum it changes its color to a deep blood-red. With solution of gold it produced a purple precipitate used in painting porcelain, and known under the name of *Purple of Cassius.* With infusion of cochineal it produces a purple precipitate; and it is much used to fix and alter colors in dyeing and calico-printing.

PERCHLORIDE OF TIN ($SnCl_2$).—If tin is heated in excess of chlorine, or if a mixture of 1 part of tin filings and 4 of corrosive sublimate is distilled, the perchloride will pass over. It is a transparent colorless fluid, formerly called *Libavius's Fuming Liquor:* it exhales copious fumes when exposed to moist air; and with one-third its weight of water it forms a crystallized hydrate =($SnCl_2 5HO$). It does not congeal at —20°. Its boiling point is 250°; and the density of its vapor is 9·19. It is instantly decomposed by metallic zinc, forming chloride of zinc and a precipitate of metallic tin. A solution of perchloride of tin much used by dyers, is made by dissolving tin in a mixture of 2 measures of hydrochloric acid, 1 of nitric acid, and 1 of water. The perchloride forms double salts with the chlorides of ammonium, potassium, and sodium.

PROTOSULPHIDE OF TIN (SnS) may be formed by heating tin with sulphur. A hydrated protosulphide of tin is precipitated from the salts of the protoxide, by sulphuretted hydrogen; it is of a brownish-black color, and loses water when heated. Sulphide of tin is a brittle black compound, soluble in hydrochloric acid with the evolution of sulphuretted hydrogen.

SESQUISULPHIDE OF TIN (Sn_2S_3) is obtained by heating the protosulphide with one-third its weight of sulphur: it is of a yellowish-gray color, metallic lustre, and when digested in hydrochloric acid gives out sulphuretted hydrogen, and leaves a yellow residue of bisulphide.

BISULPHIDE OF TIN (SnS_2) is obtained as follows: Take 12 oz. of tin and amalgamate it with 6 oz. of mercury; reduce it to powder, and mix it with 7 oz. of sublimed sulphur and 6 oz. of salammoniac, and put the whole into a glass matrass placed on a sand-bath. Apply a gentle heat till the white fumes abate, then raise the heat to redness, and keep it so for a due time. On cooling and breaking the matrass, the bisulphide of tin is found at the bottom. The use of the mercury is to facilitate the fusion of the tin and its combination with the sulphur, while the sal-ammoniac prevents such increase of temperature as would reduce the tin to the state of protosulphide. A hydrated bisulphide of tin is formed by decomposing a solution of perchloride of tin by sulphuretted hydrogen. The precipitate becomes of a dingy yellow when dried, and has a vitreous fracture.

The extraordinary golden lustre of the bisulphide of tin, and its flaky texture, rendered it an object of great interest to the alchemist: it was termed *aurum musivum,* and *mosaic gold.* When well made, it is in soft golden flakes, friable and adhering to the fingers; sp. gr. 4·4 to 4·6. It is insoluble in acids, except in nitrohydrochloric acid; it is soluble in caustic potassa, but not without partial decomposition. It dissolves in sulphide of sodium, and the concentrated solution yields crystals of a hydrated double sulphide, the formula of which is $2NaS+SnS_2+12HO$. It is used for ornamental work, under the name of *bronze-powder,* especially by the manufacturers of paper-hangings: it is chiefly imported from Holland and Germany.

Tin pyrites is a rare mineral composed of the disulphides of copper and iron with bisulphide of tin, $=2(Fe_2,S)SnS_2+2(Cu_2,S)SnS_2$.

SULPHATES OF TIN.—When excess of the tin is boiled in sulphuric acid, a solution is obtained which deposits white acicular crystals of *protosulphate of tin*. Protosulphate of tin is also precipitated by pouring sulphuric acid into protochloride of tin. When tin is boiled in excess of sulphuric acid, a *persulphate* is formed.

ALLOYS.—*Tin-plate* is a most useful alloy of tin and iron, in which iron plate is superficially combined with tin, and to the surface of which a quantity of tin further adheres, without being in combination. It is made by dipping cleansed iron plates into a bath of melted tin. An objection to such combinations is, that in consequence of the electrical relations of the metals, the iron, if anywhere exposed, has an increased tendency to oxidation: for although the surface of the tin itself is sufficiently durable, no sooner is any portion so abraded as to denude the iron, than a spot of rust appears and rapidly extends: hence the superiority of iron plate covered by zinc instead of tin, zinc being electro-positive, whereas tin is electro-negative in regard to iron, under the influence of common oxidizing agents.

Moiré métallique is tin plate which has been superficially acted on by an acid, so as to display, by reflected light, the crystalline texture of the tin: the tin plate being best suited for the purpose is that which has rather a thick coating of pure tin. It should first be well cleansed by washing its surface with a little caustic potassa, then in water, and drying it. The acid employed is always some modification of the nitrohydrochloric, more or less diluted; a mixture of 8 parts of water, 2 of nitric, and three of hydrochloric acid, generally answers well. The plate should be slightly heated, and then quickly sponged over with the acid, so as to bring out the moiré; it should then be immediately dipped into water containing a little potassa dissolved in it, well washed, and perfectly dried. If the acid has blackened or oxidized the surface, a solution of caustic potassa will generally clean it. The crystals on the unprepared tin plate are usually large and indistinct, so that it is often modified expressly for the purpose, by heating it up to the point of the fusion of the tin, powdering it over with sal-ammoniac to remove the oxide, and then plunging it into cold water; in this way the crystals are generally small. By sprinkling the surface of the heated plate with water, or by only partially fusing the tin by holding the plate over the flame of a spirit-lamp, or running a blowpipe flame over it, various modifications of the crystalline surface may be obtained, or different devices sketched as it were upon it. The plates are generally finished by a coating of transparent or colored varnish.

The *tinning of pins* is effected by boiling them for a few minutes in a solution of 1 part of bitartrate of potassa, 2 of alum, and 2 of common salt, in 10 or 12 of water, to which some tin filings, or finely granulated tin are added; they soon become coated with a film of tin, and are then taken out, cleaned and dried. The pins are made of brass wire, and require to be perfectly clean before they are put into the tinning liquor. Tin medals, or casts in tin, are *bronzed* by being first well cleaned, wiped, and washed over with a solution of 1 part of protosulphate of iron, and 1 of sulphate of copper, in 20 of water: this gives a gray tint to the surface; they are then brushed over with a solution of 4 parts of verdigris in 11 of distilled vinegar; left for an hour to dry; and polished with a soft brush and calcothar.

TESTS FOR THE SALTS OF TIN.—The *protosalts* are colorless and acid; they are generally represented by protochloride: 1. *Sulphuretted hydrogen*, and hydrosulphate of ammonia, give a deep brown precipitate of protosulphide (SnS). This is dissolved by an excess of the hydrosulphate, and is converted into bisulphide (SnS_2). Acids throw it down yellow from this solution. 2. *Potassa* gives a white precipitate (hydrated oxide), soluble in an excess of the alkali, and in hydrochlorate of ammonia. 3. *Ammonia,* and alkaline carbonates and bicarbonates produce, in diluted solutions, white precipitates, insoluble in an excess of the reagents as well as in hydrochlorate of ammonia. 4. Corrosive sublimate gives a white precipitate, becoming gray or black when heated, provided the salt of tin is in excess. This is owing to the separation of metallic mercury. 5. Chloride of gold gives, with a diluted solution, a red-brown color, which becomes of a deep purple red when heated. 6. When heated with a salt of copper, the salt is reduced to white dichloride, which is precipitated on the addition of water. A piece of granulated zinc, placed in the diluted liquid acidified, separates tin in crystals. The *persalts* of tin (perchloride): 1. *Sulphuretted hydrogen* and *hydrosulphate* of ammonia give a dingy yellow precipitate of bisulphide of tin, which is soluble in an excess of the hydrosulphate. 2. Potassa gives a white precipitate soluble in an excess of the alkali, but insoluble in hydrochlorate of ammonia. 3. Ammonia, and all alkaline carbonates give a white precipitate, insoluble in an excess and in the hydrochlorate of ammonia. 4 and 5. Corrosive sublimate and chloride of gold produce no change in the solution. In a mixture of proto and persalts, chloride of gold in small quantity, gives a deep ruby-red color, or precipitate.

CADMIUM ($Cd=56$).

This metal was discovered in 1817 by Stromeyer; he called it *Cadmium,* from καδμεία, a term formerly applied both to calamine and to the substance which sublimes from the furnace during the manufacture of brass. It is contained in certain ores of zinc, and being more volatile than zinc, passes over with the first portions of distilled metal, from which it may be separated by dissolving it in dilute sulphuric acid, and passing sulphuretted hydrogen through the solution: the sulphide of cadmium thus precipitated, is then dissolved in hydrochloric acid, and precipitated by carbonate of ammonia. This precipitate, after having been washed and dried, is mixed with charcoal, and reduced in an earthen retort; the cadmium passes over at a dull red heat.

Cadmium, in its physical properties, much resembles tin, but it is rather harder and more tenacious: it crackles when bent. Its sp. gr. is from 8·60 to 8·69. It fuses at about the temperature required by tin, and distils over a heat somewhat below redness, condensing into metallic globules: its vapor is inodorous. Air scarcely acts upon it except when heated, when it forms an orange-colored oxide, not volatile, and easily reducible. Owing to the production of this fixed oxide, the metal cannot be volatilized except in close vessels or tubes of narrow bore. A portion is always converted into yellow oxide during sublimation.

OXIDE OF CADMIUM (CdO).—Cadmium slowly dissolves in dilute sulphuric or hydrochloric acid, with the evolution of hydrogen. The oxide is best obtained by dissolving the metal in dilute nitric acid, and precipitating it in the state of carbonate, which is then washed, dried and ignited. It is of a reddish-brown or orange color, neither volatile nor fusible; but when mixed with carbonaceous matter it appears to be volatile, in consequence of its easy reduction, and the oxidation of the separated cadmium. When thrown down from its solutions by alkalies, it forms a white *hydrate,* which absorbs carbonic acid from the atmosphere, and is soluble in excess of ammonia, but insoluble in potassa and soda.

Nitrate of Cadmium ($CdO,NO_5 4HO$) forms radiated acicular crystals, which are deliquescent, and soluble in alcohol.

Chloride of Cadmium ($CdCl$) is formed by dissolving the hydrated oxide in hydrochloric acid: on evaporation, small prismatic crystals are obtained, very soluble in water; they readily fuse, and, losing water, concrete into a lamellar crystalline mass of anhydrous chloride, which, at a very high temperature, is volatile, and condenses in the form of a nacreous sublimate. It forms double salts with the alkaline chlorides.

Bromide of Cadmium ($CdBr$).—This may be procured by digesting in a tubulated retort connected with a receiver, 2 parts of cadmium in fine shavings, 1 part of bromine, and 10 of water. When the reaction has ceased, and the liquid is colorless, it may be filtered, and concentrated in a porcelain vessel. White, silky-looking prismatic crystals are deposited; they are readily dissolved by water, alcohol, and ether.

Iodide of Cadmium (CdI).—The iodide may be procured directly by a process similar to that above described for the preparation of the bromide. The proportions are, 2 parts of cadmium in fine shavings, 4 parts of iodine, and 10 parts of water. The operation is continued until the liquor is colorless. It is then evaporated, and the iodide is deposited on cooling, in white scaly crystals of a nacreous appearance. It is soluble in water, alcohol, and ether. This salt is remarkable for its fixedness, whether solid or in solution. With the bromide, it is largely used in photography. Collodion, prepared with iodide or bromide of cadmium, retains its properties unchanged for a long period.

Sulphide of Cadmium (CdS) is obtained in the form of a bright yellow powder, insoluble in ammonia and in the fixed alkalies, by precipitating the solutions of the metal with sulphuretted hydrogen, or an alkaline sulphide. It dissolves, with the evolution of sulphuretted hydrogen, in hydrochloric acid, and is not volatile at a white heat. It furnishes a yellow pigment, which mixes well with other colors, and closely resembles sulphide of arsenic.

Sulphate of Cadmium ($CdO,SO_3 4HO$) yields transparent prismatic crystals, very soluble in water, and forming a double salt with sulphate of potassa.

Carbonate of Cadmium (CdO,CO_2) is a white anhydrous powder, which loses its acid at a red heat.

Tests for the Salts of Cadmium.—1. *Sulphuretted hydrogen* gives a bright yellow, passing to an orange-yellow precipitate, even in acid solutions. This precipitate is insoluble in potassa and ammonia, but is dissolved by strong hydrochloric acid. By these properties, the sulphide of cadmium is easily distinguished from that of arsenic. 2. *Hydrosulphate of ammonia* gives a yellow sulphide, insoluble in an excess of the reagent. 3. Potassa throws down a white oxide, insoluble in an excess of the alkali, and in hydrochlorate of ammonia. 4. *Ammonia*, a white oxide, soluble in excess, not precipitated by hydrochlorate of ammonia, but thrown down as yellow sulphide by sulphuretted hydrogen. 5. *Carbonate of ammonia* and other alkaline carbonates, a white precipitate, insoluble in excess. 6. *Ferrocyanide of potassium* gives a white precipitate, insoluble in hydrochloric acid; and the *ferricyanide* a brownish-yellow precipitate, soluble in a large excess of hydrochloric acid. Zinc precipitates cadmium in its metallic state from its solutions.

CHAPTER XXXII.

COPPER AND LEAD.

COPPER ($Cu=32$).

COPPER, *Cuprum*, or *Venus*, of the alchemists (♀), was known in the early ages of the world, and was the principal ingredient in the manufacture of domestic utensils, and instruments of war, previous to the discovery of malleable iron. The word *copper* is derived from *Cyprus*, the island where it was first wrought by the Greeks. It is found *native*, and in various states of combination. The sulphides are its most abundant ores, and from them, commercial demands are almost exclusively supplied.

Manufacture of Copper.—The ore, having been picked and broken, is heated in a reverberatory furnace, by which arsenic and sulphur are in great part driven off. It is then transferred to a smaller reverberatory, where it is fused, a large portion of the sulphide of iron having been converted into oxide, which, by the addition of silicious sand, forms a vitreous slag. When the iron is thus separated, the sulphur begins to burn out of the sulphide of copper, and the copper becoming oxidized, is reduced by the carbonaceous matter. The impure metal is then granulated by letting it run into water: it is afterwards remelted and granulated two or three times successively, in order further to separate impurities, which are chiefly sulphur, iron, and arsenic; and it is ultimately cast into oblong pieces called *pigs*, which are broken up, roasted, and melted with a portion of charcoal in the refining furnace. Malleability is here conferred upon the copper, and its texture improved, by stirring the metal with a pole of green wood: assays are occasionally taken out, and the metal, originally crystalline and granular when cold, now becomes fine and close, so as to assume a silky hue when the assays are half cut through and broken. The metal is then cast into cakes. The whole process of refining copper, and toughening it by *poling*, requires much care; and if it be over-poled, the metal is even rendered more brittle than in its original state. The effect of poling has not been satisfactorily explained: it may consist in the separation of a small portion of oxide of copper; and the effect of over-poling may possibly depend upon the combination of the copper with a portion of carbon. Copper for brass-making is granulated by pouring the metal through a perforated ladle into water; when this is warm, the copper assumes a rounded form, and is called *bean-shot;* but if a constant supply of cold water is kept up, it becomes ragged, and is called *feathered shot.* Another form into which copper is cast, is in pieces of the length of six inches, and weighing about eight ounces each: the copper is dropped from the moulds, immediately on its becoming solid, into a cistern of cold water, and thus, by a slight oxidation of the metal, the sticks acquire a rich red color on the surface. This is called *Japan copper.*

Copper may be obtained by the voltaic decomposition of a solution of the sulphate; or by dissolving the copper of commerce in nitric acid, with the addition of a little sulphuric acid; the solution is diluted, and a plate of iron is immersed, upon which the copper is precipitated; after having been previously washed in dilute sulphuric acid, to separate a little adhering iron, it may be fused into a button.

The usual impurities in ordinary copper are traces of arsenic, antimony, tin, lead, iron, oxide of copper, and carbon. From recent researches it appears that all English "refined" copper, whether in the state of foil or the finest wire, contains a notable proportion of arsenic. This impurity does not affect the ductility or malleability of copper to the extent alleged by some chemical writers; but, according to Dr. Mathiessen's experiments, it diminishes to a considerable extent the conducting power of the metal in reference to electricity, so that such interference might almost be made a test of the presence of this impurity. Copper free from arsenic cannot be obtained, except with the greatest difficulty. The presence of arsenic in small quantity is easily overlooked, and thus samples which contain it are frequently sold as pure. The Burra Burra copper, as well as about forty samples of copper, British and foreign, which we have examined, contained arsenic in variable proportion. The arsenic is associated in the ore with the sulphides of iron and copper, and cannot be expelled from the metal by heat, or in the ordinary process of refining. Some coppers from America, obtained from native carbonates, have been found free from arsenic. We have, under OXIDE OF COPPER (p. 388), given a process for obtaining this metal pure; and under (SUBCHLORIDE OF COPPER (p. 390), we have described a method for the detection of arsenic in copper.

Properties.—Copper is the only metal which has a red color: it has much lustre, and is very malleable, ductile, and tenacious: it exhales a peculiar smell when warmed or rubbed. It melts at a temperature intermediate between the fusing-points of silver and gold, = 1996° Fahr., and when in fusion absorbs small quantities of oxygen, which again escape when the metal solidifies, occasioning a spirting out of portions of the liquid metal. At a very high temperature, copper emits fumes which condense upon cold surfaces into minute globules of protoxide with a metallic nucleus. Its specific gravity varies from 8·788 to 8·958; the former being the least density of cast copper, the latter the greatest of rolled or hammered copper. The sp. gr. of some samples of copper, containing a little of the protoxide, does not exceed 8·5, and such copper is of inferior ductility. When copper is in a state of extreme division, it burns like tinder; under a flame urged by oxygen gas, it burns with a green light. Exposed to damp air, copper becomes covered with a thin greenish crust of hydrated oxide and carbonate. If heated and plunged into water, a quantity of reddish scales separate, consisting of an imperfect oxide. The same scales fly off, during cooling, from a plate of the metal which has been heated red-hot. Copper does not decompose water at a red heat. It deoxidizes nitric acid (sp. gr. 1·5) rapidly in the cold. It has no action on sulphuric acid, except at a boiling temperature, when it deoxidizes this acid, and sets free sulphurous acid. Hydrochloric acid exerts no action on it in the cold, unless the metal is at the same time exposed to air; but if heated, chloride of copper is formed, and hydrogen escapes. Hydrogen, however, is only slowly eliminated, even under these circumstances, and it is commonly combined with arsenic or antimony.

Native copper occurs in a variety of forms; massive, dendritic, granular, and crystallized in cubes or octahedra. It is found in Cornwall, Siberia, Saxony, Hanover, Sweden, America, Cuba, and Australia.

COPPER AND OXYGEN.—There are two oxides of copper, a *suboxide* or *dioxide*, Cu_2O, and a protoxide, CuO: the latter is the basis of the stable and common salts of copper. The dioxide combines directly with only a few of the acids, and is in most cases resolved by them into metallic copper and the oxide: ($Cu_2O=Cu+CuO$).

SUBOXIDE OF COPPER; *Dioxide of Copper* (Cu_2O).—This oxide may be formed by adding to an aqueous solution of equal weights of sulphate of copper and sugar, a sufficiency of soda to redissolve the first precipitate, and then boiling the resulting blue liquor: the suboxide falls as a red powder, which, when washed and dried, is permanent in the air. By boiling a solution of acetate of copper with a sufficiency of grape-sugar, it is readily obtained without the addition of caustic alkali. It is yellow or orange-colored in the hydrated state, as it is at first precipitated; but it becomes anhydrous and of a deep red color, by continued boiling. This oxide occurs *native* as *Ruby copper,* crystallized in octahedra. When dioxide of copper is heated in the air, it passes into oxide. The dilute acids mostly decompose it and separate metallic copper. It dissolves in concentrated hydrochloric acid; it also dissolves in ammonia, forming a colorless solution when kept from air; but it is not soluble in solutions of potassa or of soda. Its salts are frequently formed by the action of deoxidizing agents on the protosalts.

Copper vessels, such as tea-urns, and medals, are often superficially coated with oxide, or *bronzed;* it gives them an agreeable appearance, and prevents tarnish. For this purpose two processes are resorted to. 1. The copper surface is cleaned, and then brushed over with peroxide of iron (generally colcothar) made into a paste with water, or with a very dilute solution of acetate of copper; heat is then cautiously applied in a pròper furnace or muffle, till it is found, on brushing off the oxide, that the surface beneath has acquired its proper hue. 2. Two parts of verdigris and one of sal-ammoniac are dissolved in vinegar: the solution is boiled in a pipkin, skimmed, and diluted with water until it only tastes slightly of copper and ceases to deposit a white precipitate: it is then poured into another pipkin or copper pan, and rapidly brought to boil, and the medal, previously rendered perfectly clean, is dipped into the boiling solution, which may be most conveniently done by placing it in a small perforated copper ladle. The surface of the medal becomes at first black or dark blue, and, in about five minutes, acquires the desired brown tint; it must then be instantly withdrawn and washed in a stream of water, and lastly, carefully wiped and dried. The medal is generally perfected by afterwards giving it one gentle pinch between the dies. When there are many medals, each must be bronzed separately; they must not be allowed to touch each other, and care should be taken to rest them upon as few points of contact as possible. The bronzing-liquid must not be suffered to concentrate by evaporation, but must be diluted if necessary, so as to keep it in a proper state, and especially to avoid all appearance of a white precipitation in it.

OXIDE OF COPPER.—*Protoxide* (CuO).—When sheet copper is exposed in the air to a red heat, black scales form upon it, which are thrown off on plunging it into water, or which fly off as it cools, in consequence of the comparatively rapid contraction of the metal. When these scales are reduced to powder, and stirred in contact of air at a red heat, they yield the oxide. When nitrate of copper is exposed to heat gradually raised to redness, it fuses and is decomposed, and ultimately this oxide remains. The oxide may be at once prepared in large quantity, by dissolving copper in one part of nitric acid and two parts of water, evaporating to dryness, and heating the residue to redness in a platinum dish. The arsenic contained in "refined" copper is converted into arsenic acid. It may be separated from the black oxide by boiling it in distilled water, until nitrate of silver no longer gives a red color with the residue of the evaporated water. When the purified oxide is dissolved in sulphuric acid, and the metal is precipitated by voltaic electricity, it is free from arsenic, and may be regarded as pure copper. Thus procured, it is brittle, and admits of lamination with difficulty. It requires frequent annealing to reduce it only to a moderately thin sheet.

Oxide of copper is black; its specific gravity is 6·4. Before the blowpipe, it fuses when intensely heated in the point of the flame, upon charcoal: in the interior of the flame it affords a globule of metal. Heated alone, it is not decomposed at the highest temperature, but it is easily and rapidly decomposed at a dull red heat, or even below it, by hydrogen or carbon. It is also decomposed when heated in contact with organic substances, converting their hydrogen into water, and their carbon into carbonic acid; hence its use in their analysis: it is hygrometric, and if weighed whilst hot, augments in weight after cooling, in consequence of the absorption of aërial moisture. It is insoluble in water, but it dissolves in the greater number of the acids, and is the basis of all the common salts of copper. When alkalies are dropped into its solutions, they throw it down as a bulky blue *hydrate*, which, however, is not permanent at a boiling heat, but becomes black and anhydrous when boiled in an excess of the alkaline liquid. This oxide of copper is not soluble in the liquid fixed alkalies, except in the presence of sugar, tartrate of potassa, albumen, caseine, glycerine, and some other substances. With grape-sugar and an excess of the alkaline liquid, the hydrated oxide of copper forms a rich sapphire-blue solution, which reduces the protoxide to suboxide slowly in the cold but rapidly when heated. This constitutes *Trommer's test* for sugar. Other reducing agents operate in a similar manner. Thus, if arsenious acid is present, potassa forms with the oxide, a blue solution which, when boiled, yields, like sugar, a hydrated or anhydrous suboxide of copper. When carbonate of potassa or of soda is fused with it, it expels carbonic acid, and combines to form a blue or green compound. Its combination with ammonia will presently be noticed. It communicates a green, and sometimes a blue tint to vitreous compounds; and is the basis of certain colors used by the ancients, which had been supposed to contain cobalt.

Hydrated Oxide of Copper (CuO,HO), as thrown down from a solution of sulphate of copper by dilute potassa or soda, is at first blue, but soon changes to green, especially if it be dried: it sustains, when dry, a temperature of 212° without decomposition, but a little above that it becomes discolored. When boiled in the liquor from which it has been precipitated, or when a solution of copper is added to a boiling solution of soda or potassa, it becomes anhydrous and nearly black.

NITRATE OF COPPER ($CuO,NO_5,3HO$).—Nitric acid diluted with 3 parts of water, rapidly oxidizes copper, evolving nitric oxide, and ultimately forming a bright-blue solution, which affords deliquescent prismatic crystals, of a fine blue color, very soluble in water and in alcohol. They liquefy at a temperature below 212°; at a higher temperature they lose water and acid, becoming a *subnitrate*, and are entirely decomposed at a red-heat, leaving protoxide of copper.

At low temperatures this salt crystallizes in rhomboidal plates, which contain 6 atoms of water, but these effloresce into the terhydrate *in vacuo* over oil of vitriol. Potassa forms, in the solution of this nitrate, a bulky blue precipitate of hydrated oxide of copper, which, as already observed, when boiled in potassa or soda, becomes black from the loss of its combined water. When nitrate of copper is coarsely powdered, sprinkled with a little water, and quickly rolled up in a sheet of pure tinfoil, there is great heat produced, nitrous gas is rapidly evolved, and the metal often takes fire. Ammonia added to a solution of nitrate of copper, occasions a precipitate of the hydrated oxide; but if added in excess, the precipitate is redissolved, and an *ammonio-nitrate* is produced.

AMMONIA AND OXIDE OF COPPER.—When copper filings are digested in aqueous ammonia exposed to air, the solution soon becomes blue: if air be then excluded, it gradually loses color, but again acquires a blue color on the contact of air: in the blue liquor the copper exists as *oxide;* in the colorless liquor as *dioxide.* If a tall glass be filled with liquid ammonia and a few drops of solution of suboxide of copper (subchloride) are added, the surface becomes blue, but it remains colorless below. The solution of the oxide of copper in ammonia is obtained by exposing copper filings in solution of ammonia to air, or by dissolving the hydrated oxide in ammonia: it is of a splendid deep-blue color.

COPPER AND CHLORINE.—Gaseous chlorine acts upon finely-divided copper with great energy, producing the phenomena of combustion; *two* chlorides are the result of this action; the one a comparatively fixed fusible substance, which is the *subchloride:* the other a yellow substance, which is a *chloride.*

SUBCHLORIDE OF COPPER.—*Dichloride* (Cu_2Cl) may be obtained by exposing copper filings to the action of chlorine, not in excess: or by evaporating the solution of dioxide of copper in hydrochloric acid, and heating the residue in a vessel with a very small orifice; or by heating the protochloride in the same way. It is also precipitated, on adding protochloride of tin to a strong solution of the chloride. It is insoluble in water, but soluble in ammonia—a solution employed in eudiometry. It is also dissolved by hydrochloric acid, from which potassa throws down the hydrated dioxide: when water is added to its hydrochloric solution, it is thrown down in the form of a white granular or crystalline hydrate: its color varies, being brown when fused, but if slowly cooled, it is yellow, translucent, and crystalline; when in fine division it is nearly white: it must be preserved out of contact of air. If moistened and exposed to air, it acquires a green color, and becomes converted into a hydrated oxychloride, which has been termed *submuriate of copper*, or *Brunswick green;* the same compound may be formed by adding hydrated oxide of copper to a solution of the chloride; or by exposing to the atmosphere slips of copper partially immersed in hydrochloric acid. In this case, the following changes first take place: $HCl+2Cu+O$ (air)$=Cu_2Cl+HO$. A portion of the metal becomes oxidized, and the oxychloride results. A mixture of this kind was employed by Gay-Lussac in the analysis of the atmosphere, and it serves as a process for obtaining nitrogen (p. 141). After 24 hours the acid liquid in which the copper has been partially immersed, acquires a dark greenish-brown color from the production of dichloride. In this state, if the liquid is submitted to distillation at a moderate temperature, any arsenic present in the copper will be distilled over with hydrochloric acid, as chloride of arsenic (*see* ARSENIC). By evaporating this subchloride to dryness, the whole of the arsenic may be driven off; and by further exposure in contact with pure hydrochloric acid, pure oxychloride of copper may be obtained. As these precautions are not taken in practice, the oxychloride, as it is generally prepared, contains arsenic.

CHLORIDE OF COPPER ($CuCl$) may be formed by heating copper filings in excess of chlorine, or by dissolving oxide of copper in hydrochloric acid, and evaporating to dryness by a heat below 400°. Chloride of copper is brown when anhydrous, but becomes blue by exposure to air; it is soluble in water and alcohol, and very difficultly crystallizable. The prismatic crystals are $CuCl,2HO$. The concentrated aqueous solution is green; when diluted, blue; but the solution again becomes green when heated to 212°. Exposed to a red heat in a tube with a small orifice, chlorine is expelled, and it becomes a subchloride. When acted upon by potassa not added in excess, and only so as partially to decompose it, a green oxychloride is thrown down.

Oxychloride of Copper, $3(CuO)CuCl,4HO$, is found *native* in Peru and Chili, sometimes in the form of green sand, and sometimes massive and crystallized. The *green sand* was first found in the desert of Atacama, separating Peru from Chili. Chloride of copper has also been found upon some of the lavas of Vesuvius.

SUBIODIDE OF COPPER; DINIODIDE OF COPPER (Cu_2I).—When iodide of potassium is added to a solution of the protosulphates of copper and iron, both in crystals, in the proportion of 1 to 2¼, the protoxide of iron takes the oxygen of the oxide of copper, and the iodine the metallic copper, with which it forms a white precipitate of the insoluble diniodide; it may be dried in close vessels. In the manufacture of iodine the mixed sulphates are sometimes employed for precipitating the iodine from the iodides in kelp (p. 189). When iodide of potassium is added to a salt of oxide of copper, iodine is set free, and a brown subiodide falls.

COPPER AND SULPHUR; DISULPHIDE OF COPPER (Cu_2S) may be formed by heating a mixture of 8 parts of copper filings and 3 of sulphur: as soon as the latter melts the copper becomes red-hot, undergoes combustion, and a black brittle compound is formed. It is soluble in hydrochloric acid with the evolution of sulphuretted hydrogen. *Vitreous copper* is a native disulphide; it occurs crystallized and massive in Cornwall and Yorkshire. It has a gray color, a metallic lustre, and a sp. gr. of about 5·7.

SULPHIDE (CuS) occurs *native*, associated with the disulphide. It is thrown down from solutions of salts of copper by sulphuretted hydrogen, as a dark-brown hydrate, insoluble in alkalies and diluted acids.

Ferrosulphides; Copper pyrites, or *yellow copper ore* is the ore from which commercial copper is chiefly derived. It is a compound of sulphur, copper, and iron, the proportions of the sulphides being subject to variation, but commonly represented by Cu_2S,Fe_2S_3.

SULPHATE OF COPPER; ROMAN VITRIOL; BLUE VITRIOL (CuO,SO_3).—This salt is formed by boiling copper in sulphuric acid, a process which furnishes an abundance of sulphurous acid ($Cu+2SO_3=CuO,SO_3+SO_2$). It is also made by exposing roasted sulphide of copper to air and moisture; thus obtained, it is impure, generally containing iron, and often zinc. It is obtained in large quantities, and nearly pure, in certain processes, afterwards to be described for refining gold and silver.

Sulphate of copper forms rhomboidal crystals (containing 5 atoms of water, ($CuO,SO_3,5HO$): sp. gr. 2·27. The crystals are sometimes very large, of a beautiful sapphire-blue color, and slightly efflorescent in a dry atmosphere; they are soluble in 4 parts of cold water. This salt has a peculiarly nauseous metallic taste. When heated to 212°, it loses 4 atoms of water of crystallization, and crumbles down into a pale powder; heated to 400° it becomes white and anhydrous; in this state it slowly reabsorbs water from the air, and regains its blue color; or if sprinkled with water heat is evolved, and the salt crumbles down into a blue hydrate. By a continued high red or white heat, sulphuric acid, and some sulphurous acid and oxygen, are evolved, and black oxide of copper remains. Anhydrous sulphate of copper, by reason of its great affinity for water, removes it from liquids, such as alcohol, ether, chloroform, and pyroxylic spirit. It is occasionally used in dehydrating these liquids by distillation. The powder changes in color from white to blue. When the blue crystals of the salt are digested in concentrated sulphuric acid, they are dehydrated and become white. This salt (the *Vitriol*, or *Salt of Venus*, of the alchemists) is much used as a source of several blue and green colors. It is employed by dyers and calico-printers, and is an ingredient in some kinds of writing-ink. It has been used to prevent smut in corn, by steeping the grain in a dilute solution of the salt. It is also employed to prevent *dry rot* by steeping timber or planks in its solution; and it is a powerful preservative of animal substances. The commercial sulphate sometimes contains sulphate of iron as impurity. In order to detect this, ammonia may be added to the diluted solution of sulphate in sufficient quantity to redissolve the whole of the oxide of copper which is at first precipitated. As oxide of iron is not permanently dissolved by ammonia, this after some hours will be deposited as hydrated peroxide at the bottom of the tube. There is, however, a more serious impurity—namely, the presence of arsenic—not only in the commercial but the official sulphate. This may be detected by distilling the powdered crystals with strong hydrochloric acid. Chloride of arsenic passes over into the receiver (*see* Arsenic). Several basic sulphates of copper have been described.

Sulphates of Ammonia and Copper.—1. *Ammonio-sulphate of copper.* Anhydrous sulphate of copper rapidly absorbs gaseous ammonia, heats, and forms a bulky blue powder soluble in water, $=5NH_3, + 2(CuOSO_3)$. 2. *Cuprosulphate of ammonia.* When a solution of sulphate of copper is supersaturated by ammonia so as to redissolve the precipitate at first formed, and crystallized by evaporation, dark, blue transparent crystals are obtained, soluble in 1·5 of cold water, but insoluble in alcohol, $= CuO,SO_3 + 2NH_3HO$. The crystals, when exposed to air, lose ammonia, becoming at first opaque and pale blue, and then crumble into a green powder, which is a mixture of sulphate of ammonia and basic sulphate of copper. When the aqueous solution of this salt is largely diluted, it deposits basic sulphate of copper. 3. *Sulphate of ammonia and copper.* $(NH_4O,SO_3 + CuO,SO_3 + 6HO)$. This salt crystallizes out of the mixed solution of sulphate of ammonia with sulphate of copper; it effloresces in dry air. The solution of the ammonio-sulphate of copper is used as a test for arsenic.

Carbonates of Copper.—When hot solutions of copper are precipitated by the carbonated fixed alkalies, carbonic acid is evolved, and a bulky green *hydrated dicarbonate of copper* falls, $= 2(CuO),CO_2,HO$. Its tint is improved by repeated washing with boiling water. It is prepared as a pigment, under the name of *mineral green*, or *green verditer.* When a cold dilute solution of sulphate of copper is decomposed by carbonate of soda, a blue precipitate falls, which, by careful drying, retains its color, and is known under the name of *blue verditer.* It differs from the green carbonate in containing more water. There is an inferior pigment, also called *verditer*, which is a mixture of subsulphate of copper and chalk.

Native Carbonates of Copper; Malachite (*μαλάχη, mallow*, from its color), or the *green hydrated carbonate*, $= 2(CuO),CO_2,HO$, is found in various forms, but never regularly crystallized, the octahedral variety being a pseudo-crystal derived from the decomposition of the red oxide: it occurs in great beauty in a stalactitic form in Siberia, and in Australia; it is rarely found in Cornwall. It is of various shades of green, and often cut into small slabs, or used as beads and brooch-stones. The pulverulent variety has been termed *chrysocolla*, and *mountain-green.* The *blue hydrated carbonate*, $= 3(CuO)CO_2,HO$, is found in great perfection at Chessy, near Lyons. It occurs crystallized in rhomboids and imperfect octahedra; it is also found in small globular masses. The earthy variety is sometimes called *copper-azure* or *mountain-blue.* The *dioptase*, or *copper emerald*, a rare mineral, hitherto found only in Siberia, is a *hydrated silicate of copper;* some of the varieties of malachite also appear to contain a silicate of copper.

Cyanide of Copper.—Hydrocyanic acid, and cyanide of potassium, throw down a white curdy precipitate in a solution of dichloride of copper, $= Cu_2$, Cy. It combines with other metallic cyanides, forming a class of *cuprocyanides.* When cyanide of potassium is added to sulphate of copper, a brown precipitate,$=$CuCy is formed, which by giving off cyanogen passes into a double cyanide,$=Cu_2$,Cy$+$CuCy. When CuCy is digested in excess of cyanide of potassium, it forms two *cuprocyanides,* CuCy,KCy, and CuCy, 3KCy.

Alloys of Copper.—Many of these are of great use in the arts, especially those with zinc and tin, and with silver and gold.

Brass.—This important alloy of copper with zinc was formerly made by mixing granulated copper with calamine and charcoal, and exposing the mixture to a heat sufficient to reduce the calamine and melt the alloy. It is now usually prepared by melting granulated copper with about half its weight of zinc, but the relative proportions of the two metals vary in the different kinds of brass; and some contain a little lead and tin. An alloy of 54 parts of zinc and 46 of copper is white and crystalline, but it assumes the yellow color of brass when the zinc is increased, as well as when it is diminished. Ordinary brass contains about 64 per cent. of copper. Muntz's *patent sheathing metal,* which has been found an excellent substitute for copper, is an alloy of about 60 copper and 40 zinc: it admits of being rolled hot, whereas the common varieties of brass generally split under such circumstances, and are therefore rolled cold, which requires more time.

Brass is very malleable and ductile (when cold), and its color recommends it for many purposes of the arts: its specific gravity varies from 7·9 to 8·9, and exceeds the mean of its components. *Tutenag, Tombac, Dutch gold, Similor, Prince Rupert's metal, Pinchbeck,* and *Manheim gold,* are alloys containing more copper than exists in brass, and consequently made by fusing various proportions of copper with brass. An alloy of 576 parts of copper, 59 of tin, and 48 of brass, is equal to brass in hardness, and may be worked with the same facility; it has been used for standard measures, as being less liable than brass to oxidation when exposed to air.

Speculum metal is an alloy of copper and tin, with a little arsenic; about 6 copper, 2 tin, 1 arsenic. The Earl of Rosse employed copper and tin only in the speculum of his large telescope; the proportions he used were 126·4 of copper, to 58·9 of tin (about 4 atoms of copper to one of tin).

Bronze; Bell-metal.—These are alloys of copper and tin; they are harder and more fusible, but less malleable than copper. The specific gravity of bronze exceeds the mean of its component metals, when carefully hammered and free from air-blebs: but bronze castings are apt to be porous unless considerable care and skill have been used in fusing and pouring the metal, and in the construction of the mould; and in large castings, owing to the gradual cooling of the mass, there is often a want of uniformity in the composition of different parts of it; that portion containing the least tin being the first to solidify, while the more fusible portion to a certain extent separates, and is sometimes projected from the mould.

In large bronze castings, such as statues, porosity and bubbles require carefully to be avoided: where they exist so as to deface the appearance of the work, they are sometimes filled up with substances which are only temporarily durable, or which, if metallic, give rise to electrical effects which time renders prejudicially evident. For this reason, the different pieces of a large statue should be fused together, or united by bronze, and not by a mere fusible solder; and iron bars, and leaden junctions for the support or fixing of the work, should, upon the same principle, be avoided, as they are themselves liable, under such circumstances, to corrosion, and this may affect the stability or safety of the statue, independently of other influences. Of the difficulty of casting a large and perfect bell in bronze, the Great Bell at Westminster has furnished a memorable instance.

When bronze is frequently remelted it gradually loses tin by oxidation, so that in such cases fresh additions of tin may sometimes be requisite; and it is apparently this oxidation of the tin which tends to deteriorate the texture of remelted bronzes, and renders them more subject to bubbles and porosity when recast, an effect which may be prevented by the action of carbonaceous fluxes, or by the operation of poling, as in the case of copper.

Tempering produces upon bronze an effect directly opposite to that upon steel; and in order to render bronze malleable, it must be heated to redness and quenched in water. The alloy which thus acquires the greatest tenacity is that of 8 of copper and 1 of tin, and this is consequently preferable for medals; the advantage of bronze over copper for these purposes being hardness, and resistance to oxidation; the former quality resists friction, and the latter has handed down to us the works of the ancients with little deterioration, though buried for ages in damp soil, or immersed in water. The small value of bronze, as compared with gold and silver, is also another important consideration, as affecting the preservation of such works of art. The alloy employed in the recent bronze coinage is composed of 95 copper, 4 tin, 1 zinc. The pound avoirdupois is coined into 48 pence, each piece weighing 145·83 grains; into 80 halfpence, each weighing 87·50 grains: into 160 farthings, each weighing 43·75 grains.

The analysis of brass is best effected by the action of nitric acid. The solution may be tested for the presence of lead by sulphuric acid: if tin is present it is converted into an insoluble oxide: the clear nitric solution evaporated to dryness leaves nitrate of copper and nitrate of zinc: this residue, redissolved, may be decomposed by a slight excess of caustic potassa, and boiling, by which the oxide of copper is thrown down. The oxide is collected on a filter, washed, dried, and gently ignited, the clear filtrate holds the oxide of zinc in solution: it may be neutralized by hydrochloric acid, and precipitated by carbonate of soda; the precipitate, after washing, drying, and ignition, is oxide of zinc.

Tinned Copper.—Vessels of copper for culinary purposes are usually coated with tin, to prevent the food being contaminated by copper. Their interior surface is first cleaned, then rubbed over with sal-ammoniac: the vessel is then heated, a little pitch spread over the surface, and a bit of tin rubbed over it, which instantly unites with and covers the copper. Much care is requisite in the manipulations of this process, and independently of the tin permanently adhering to and combining with the surface of the copper, there is generally a portion in excess, which fuses off, the first time the pan is used for frying. Lead is sometimes added to the tin used in tinning, and sometimes a small quantity of mercury, but these are very objectionable additions.

TESTS FOR THE SALTS OF COPPER.—The solution of these salts have either a blue or green color, and an acid reaction. 1. *Sulphuretted hydrogen* and hydrosulphate of ammonia give, even in acid solutions, a brownish-black precipitate, not soluble in the precipitants, in alkalies, or diluted acids. 2. *Ammonia*, when added in excess, produces a deep blue solution. 3. *Ferrocyanide of potassium* produces a deep red-brown precipitate in strong solutions, but a red color in those which are very dilute. This may be regarded as a most delicate test for copper. The blue ammoniacal solution above mentioned under 2, when rendered feebly acid by the addition of dilute sulphuric acid, will give a red precipitate with the ferrocyanide. Thus two of the most important tests may be applied to the same portion of liquid. 4. A polished needle, or any clean surface of iron, is coated with a layer of metallic copper of its usual red color, when immersed or suspended in the solution slightly acidified with sulphuric acid. The deposit takes place slowly when the solution is very dilute. The needle, with the red deposit, when washed and placed in a tube with a small quantity of solution of ammonia, imparts a blue color to the liquid by the production and solution of the oxide. A coil of fine steel wire may be used in place of a needle.

Before the *blowpipe*, black oxide of copper is not altered by the exterior flame, but becomes red suboxide in the interior. With borax it forms a green glass, while hot, which becomes blue-green as it cools. When strongly heated on charcoal in the interior flame, the metal is reduced.

Analysis in cases of poisoning.—A colored liquid containing organic matter, and suspected to contain copper in solution, may be thus treated: Place a portion of the liquid, acidified with dilute sulphuric acid, in a platinum capsule; touch the platinum through the liquid with a piece of zinc foil; a bright layer of metallic copper, of a red color, will be deposited on every part of the platinum touched by the zinc. Wash out the capsule with distilled water; dissolve the film of deposited metal in a few drops of nitric acid and water; expel any excess of acid, and add ammonia, and subsequently ferrocyanide of potassium (p. 394). The blue and red colors will at once indicate the presence of copper. This is the best method of proceeding in cases of poisoning; as the metal is first obtained and converted into a salt, when the tests give the results described, there can be no doubt of the presence of copper.

In order to procure a solution of the metal, the organic matter may be dried, incinerated in platinum, and the ash digested in 1 part of nitric acid and 2 of water. Pickles or fruits suspected to contain copper may be treated by the following process: Pass a bright needle through the substance; if it is impregnated with copper, there will be a deposit of this metal upon the iron. It will be proper to state in this place, that as copper and, generally speaking, all its salts, may contain arsenic, this poison may be found in an organic liquid, or in a cupreous medicine, as the result of impurity.

LEAD ($Pb=104$).

Lead has been known from the earliest ages. The alchemists gave to it the symbol and name of Saturn, ♄. The native compounds of lead are numerous, but the most important is the *sulphide* known under the name of *galena*, from which the greater proportion of commercial lead is obtained.

Extraction of Lead.—The reduction of galena upon the large scale is effected by heating and raking the prepared ore, mixed with a little lime, in a reverberatory furnace: a large proportion of the sulphur is in this way burned off, and a mixture of oxide, sulphate, and sulphide of lead obtained; the temperature is then so raised as to fuse this mixture, when the substances further react upon each other, and metallic lead separates from the mass. If it contains tin or antimony, it is further *refined* by fusing it in a shallow vessel, when those metals, being more easily oxidized than lead, are removed from the surface. If the lead contains *silver* in such proportion as to render it worth separating, this is effected by dipping into the fused metal, during cooling, a large perforated iron ladle, whereby the lead, which is the first to separate in crystals, is removed. The granular crystals are ladled out, and are nearly pure lead (p. 26), the silver being retained in the more fusible portion. By a repetition of this process the silver gradually accumulates in the latter, from which it is subsequently separated by *cupellation.* Six tons of lead thus treated, were desilvered by this process in about two hours, the weight of the argentiferous alloy left in the melting-pan being seven hundred weight. The iron ladle employed held about one hundred weight of liquid metal. The amount of silver in the lead was increased twentyfold, one ton of the alloy containing as much silver as twenty tons of the original lead. In the factory at Newcastle, in which we witnessed this operation, 60 tons of lead were desilvered weekly, producing about 600 ounces of silver. In 1858, it was calculated that the quantity of silver thus extracted from lead in this country was not less than 600,000 ounces per annum. This valuable process was discovered by the late Mr. H. L. Pattinson, of Newcastle. The lead, thus deprived of its silver, is improved in quality, and is cast into the oblong masses, or *pigs*, in which it occurs in commerce.

When lead containing silver is exposed at a high heat to a current of air, the lead is converted into protoxide, and may be run off in a fused state from the surface; whilst the silver, which, under these circumstances, resists oxidation, ultimately remains upon the cupel. This operation closely resembles that which is conducted upon a small scale by the *assayer*, and will again be adverted to in the chapter on SILVER.

The proportion of silver contained in argentiferous galena varies very considerably. The average is about ten ounces in the ton: when it amounts to 120 ounces to the ton, it is considered very rich; but silver may be profitably extracted when as low as from 3 to 4 ounces to the ton. The English lead-mines afford an annual produce of from 60,000 to 70,000 tons of metal, from the greater part of which the silver is extracted by the process above described.

Perfectly pure lead may be obtained either by reducing pure nitrate of lead by charcoal, at a red heat, or by heating oxalate of lead in a covered crucible. Its color is bluish-white: it has much brilliancy, is remarkably flexible and soft, and leaves a dark streak on paper; when handled it exhales a peculiar odor. Its specific gravity is 11·4. It admits of being rolled into thin sheets, and drawn into moderately fine wire, but its tenacity is so low as to render the latter operation difficult. It melts in about 612°, and by the united action of heat and air is readily oxidized. In perfectly close vessels it does not sublime at a bright read heat; but before the oxygen blowpipe it boils when heated to whiteness, and is dissipated in copious fumes of oxide. When slowly cooled it forms octahedral crystals, and contracts during solidification; in bullets, therefore, and in castings of lead rapidly cooled, there is generally a cavity which interferes with the rectilinear passage of the ball.

At common temperatures, and in its ordinary state, lead undergoes little change; but when in a state of very fine division, as it is obtained by exposing *tartrate of lead* to a red heat in close vessels, it takes fire when brought into the contact of air; so also the finely-divided lead obtained by the reduction of the oxide by hydrogen at a temperature insufficient for its fusion, burns when gently heated in the air. In distilled water, free from air, and in close vessels, a clean surface of lead remains bright; but in open vessels it tarnishes, and small crystalline scales of hydrated oxide of lead are formed, a portion of which dissolves in the water, and is again slowly precipitated in the form of oxycarbonate. This oxycarbonate is itself very insoluble, so that if water holding a little oxide of lead in solution be exposed to air, the more soluble oxide passes into the state of the less soluble oxycarbonate; and after a few hours, if the water be filtered, it will be found almost absolutely free from lead in solution, pure water not dissolving more than about one four-millionth of its weight of this oxycarbonate, or about one-sixteenth of a grain in a gallon. The action of water upon lead is much modified by the presence of saline substances. It is increased by chlorides and nitrates, and diminished by carbonates, sulphates, and phosphates, and especially by carbonate of lime, which, held in solution by excess of carbonic acid, is a frequent ingredient of spring and river water. But water highly charged with carbonic acid may become dangerously impregnated with lead, in the absence of any protecting salt, in consequence of its solvent power over carbonate of lead. In general, water which is not discolored by sulphuretted hydrogen, may be considered as free from lead; but there are very few waters which have passed through leaden pipes, or have been retained in leaden cisterns, in which, a minute analysis will not detect a trace of the metal; and were it not for the great convenience of lead, iron pipes and slate cisterns would, in a sanitary point of view, be in all cases preferable.

Another cause of contamination by lead may arise from electric action, as where iron, copper, or tin, is in contact with, or soldered into lead: and in these cases, owing to the action of alkaline bases as well as of acids upon the lead, danger may occur when it is thrown into an electro-negative as well as an electro-positive state. Cisterns are sometimes corroded, and their bottoms are perforated by pieces of mortar having dropped into them, the lime of which has caused the oxidation of the metal and a solution of the oxide.

OXIDES OF LEAD.—There are four definite combinations of lead and oxygen, namely, *suboxide* or *dioxide* (Pb_2O); a *protoxide* (PbO); an intermediate oxide generally known as *red oxide* (Pb_3O_4); and a *peroxide* (PbO_2). Of these, the protoxide only is salifiable.

SUBOXIDE OF LEAD; DIOXIDE OF LEAD (Pb_2O). When *oxalate of lead* is carefully heated to about 570° in a small retort, carbonic oxide and carbonic acid are evolved, and this oxide remains in the form of a gray powder, which is resolved by acids into protoxide and metallic lead.

PROTOXIDE OF LEAD (PbO) is formed, 1. By raising the temperature of melted lead to a white heat, when it burns with a brilliant flame, and forms copious fumes of protoxide. 2. By exposing the gray powder which gradually collects upon the surface of melted lead, to the further action of heat and air, until it acquires an uniform yellow color. 3. By exposing nitrate or carbonate of lead to a dull red heat out of contact of air, and taking care to avoid fusion. 4. When a solution of acetate of lead is dropped into a solution of ammonia, the white crystalline powder which falls is a *hydrated oxide.*

When this oxide is heated it has a red color, but in its ordinary state it is lemon or orange-yellow, according to the mode in which it has been prepared, and is known under the name of *Massicot.* At a high red heat it fuses and forms, on cooling, a lamellar vitreous mass of a reddish-brown color: this is often obtained in scales, under the name of *Litharge* (λίθος ἄργυρον, silver stone), which, when red from the presence of minium, was called *Litharge of Gold,* the paler varieties being termed *Litharge of Silver.* Protoxide of lead is a salifiable base, forming neutral salts with the acids; and, in many instances, subsalts which have an alkaline reaction; it absorbs carbonic acid from the atmosphere, and gradually acquires the property of dissolving in acids with effervescence. It is soluble in potassa and soda, forming yellow liquids, which after a time gradually deposit crystals of anhydrous oxide of lead: it combines with baryta, strontia, and lime, forming compounds of sparing solubility, and easily decomposed even by the weakest acids. A paste or wash containing hydrate of lime mixed with 80 to 90 per cent. of oxide of lead, is used to blacken hair, which it does in consequence of the formation of a black sulphide arising out of the combination of the sulphur in the hair with the metal of the oxide, while the lime, by its action on the organic matter, promotes the effect. The use of this compound is liable to give rise to an attack of lead palsy.

When oxide of lead is fused with the earths and metallic oxides, it forms vitreous, and in some cases very fusible compounds, hence its use in the manufacture of glass (p. 316); hence also the readiness with which it corrodes common crucibles when kept in fusion in them. Heated with charcoal, this and the other oxides of lead are easily reduced to the state of metal; they are also reduced when heated in hydrogen or coal gas.

The *hydrated* oxide, when dried at about 100°, is a soft crystalline powder, $=3(PbO)HO$: it is slightly soluble in pure water, and the solution has an alkaline reaction; it loses water and gradually becomes anhydrous when heated to about 160°. The influence of carbonic acid and minute portions of saline substances upon the solubility of this hydrate, has been above noticed.

RED OXIDE OF LEAD; MINIUM; RED LEAD (Pb_3O_4).—This substance, which is well known as a red pigment, sp. gr. between 8·6 and 9, is made by exposing protoxide of lead to heat and air so as to oxidize without fusing it, the temperature required for this purpose being between 570° and 580°; it gradually acquires a fine red color, the splendor of which, however, goes off by exposure to light. The minium of commerce is of variable composition, and generally contains excess of protoxide, which may be separated by very dilute acetic acid, or by digestion in solution in acetate of lead. When exposed to a temperature above that required for its formation, minium gives off oxygen, and reverts to the state of protoxide. The most brilliant minium is obtained by heating and stirring pure carbonate of lead in a current of air at a temperature a little short of 600°.

Minium is easily decomposed by the acids; nitric acid resolves it into insoluble peroxide, while a soluble nitrate of the protoxide is at the same time formed. Hydrochloric acid, in small quantity (2 atoms to 1 of minium), produces with it chloride and peroxide of lead, and water—$Pb_3O_4+2HCl=2(PbCl+PbO_2+2HO)$: in larger quantity, the products are, chloride of lead, water, and free chlorine; $Pb_3O_4+4HCl=3PbCl+4HO+Cl$. With an aqueous solution of chlorine it affords chloride and peroxide of lead; ($Pb_3O_4+Cl=PbCl+2PbO_2$).

PEROXIDE OF LEAD; BINOXIDE OF LEAD; PLUMBIC ACID (PbO_2).—This oxide is obtained in the form of an insoluble brown powder, by digesting minium in cold nitric acid; or by heating salts of lead with chloride of soda or lime; or by passing chlorine through minium diffused in water, or through a solution of acetate of lead, and thoroughly washing the product in hot water to remove the chloride of lead. The first is the best process, if the minium and nitric acid are pure; the resulting oxide only requires to be boiled in very dilute nitric acid, then washed, and dried at 212°.

This oxide is a conductor of electricity. At a red heat it gives off oxygen, and is converted into protoxide. By the continued action of light, or of a gentle heat, it is resolved into oxygen and minium. Digested in liquid ammonia, a mutual decomposition takes place, and water and nitrate of lead are formed. Triturated with a fifth of its weight of sulphur, it inflames spontaneously; or with half its weight of sulphur when touched with oil of vitriol. It is also decomposed, with the evolution of heat, when rubbed with an eighth part of its weight of sugar; or with its weight of crystallized oxalic acid, with which it forms water, carbonic acid, and carbonate of lead. With hydrochloric acid, it furnishes chlorine and chloride of lead. When boiled in nitric or sulphuric acid, oxygen is evolved and salts of the protoxide are formed. It absorbs sulphurous acid gas with the evolution of much heat, or even with ignition, and forms sulphate of lead; hence its occasional use in the analysis of gaseous mixtures, to separate sulphurous from carbonic acid gas. It is supposed to contain the second equivalent of oxygen in the form of ozone (p. 103). It decomposes a solution of iodide of potassium and bleaches sulphate of indigo.

Plumbate of Potassa.—When potassa, moistened with a little water, and peroxide of lead are heated for a short time in a silver crucible, a compound is obtained which, dissolved in a small proportion of water and slowly evaporated, yields crystals $=KO,PbO_2,3HO$: they are deliquescent rhomboids, soluble without decomposition in solution of potassa, but resolved by water into hydrated peroxide of lead, and a brown solution of *biplumbate of potassa. Plumbate of Soda* may be obtained in the same way, but it is little soluble in water. The insoluble plumbates are formed by heating mixtures of the bases with protoxide of lead, in the air, when oxygen is absorbed. *Plumbate of lime* and of *baryta* are so formed. Under this aspect minium is a plumbate of lead, $=2(PbO),PbO_2$.

Metallo-chromes.—When solutions of the salts of lead are electrolzyed, they deposit the peroxide on the positive electrode. When *thin films* of peroxide of lead are thus formed upon polished steel plates, they give rise to the prismatic tints described under the above name.

HYPONITRITE OF LEAD (*Tetranitrite of Lead*).—When 1 part of neutral nitrate of lead and 2 of metallic lead are boiled together for 12 hours in a large quantity of water, the filtered solution yields red crystals, alkaline to tests, soluble in about 1200 parts of cold and 34 of boiling water $=4(PbO),NO_3,HO$.

NITRITE OF LEAD.—When 166 parts (1 atom) of neutral nitrate of lead, and 156 of metallic lead (1·5 atom), are boiled in a large proportion of water, the yellow filtrate yields orange-colored crystals, soluble in 1250 of cold, and 34 of boiling water $=7(PbO),2NO_4,2HO$. When 166 parts of neutral nitrate of lead and 104 of lead (1 atom and 1) are digested together in water at about 160°, the solution deposits yellow crystals, acid to litmus, soluble in 80 parts of water at 77° $=2(PbO),NO_4,HO$.

NITRATE OF LEAD (PbO,NO_5) is obtained by dissolving the metal (or better, litharge) not in excess, in hot nitric acid diluted with two parts of water, and evaporation. It crystallizes in octahedra, which are white, anhydrous, translucent, and of a styptic taste; they decrepitate when heated, and give out nitrous acid and oxygen, and protoxide of lead remains: they are soluble in between 7 and 8 parts of water at 60°: they are insoluble in alcohol and in nitric acid. Soft wood, or paper, impregnated with this salt, burns like a slow match, with slight deflagration. Nitric acid forms with oxide of lead a dinitrate, trisnitrate, and a sexbasic nitrate.

CHLORIDE OF LEAD ($PbCl$).—When laminated lead is heated in chlorine, the gas is absorbed, and a *chloride of lead* results. The same substance is obtained by adding hydrochloric acid, or a solution of chloride of sodium, to a concentrated solution of nitrate of lead, washing the precipitate in cold water, and drying at 212°; it is also formed when the oxides of lead are digested with heat in hydrochloric acid. It is white and fusible, and, on cooling, forms a hornlike substance (*plumbum corneum*). It does not absorb ammonia. It volatilizes at a high temperature, provided air has access, in which case a portion of oxide of lead is also formed. It dissolves in about 40 parts of water at 212°, separating, as its solution cools, in small anhydrous acicular crystals, unchanged by exposure to air, and of a sweetish taste. Its solubility in water is greatly diminished by the presence of a little hydrochloric acid, yet it is soluble in strong hydrochloric acid, and is precipitated on dilution. It dissolves rather copiously in solutions of potassa and soda, and of the alkaline hyposulphites. It is insoluble in alcohol.

Native chloride of lead occurs amongst the products of Vesuvius, in small acicular crystals; a *dichloride of lead* (Pb_2Cl) has been found in the Mendip-hills, in Somersetshire; it forms fibrous yellow crystalline masses, upon a black ore of manganese; a *native oxychloride of lead* has also been found in the same locality.

OXYCHLORIDE OF LEAD.—When chloride of lead is heated in the air till it ceases to give off fumes, a compound remains $=PbCl+PbO$; it may also be formed by fusing together atomic equivalents of chloride and oxide, or chloride and carbonate of lead: it is a yellow crystalline compound. A hydrated compound of chloride and oxide of lead is obtained by acting upon a solution of common salt by litharge; solution of soda, and oxide and chloride of lead are formed; this insoluble residue, when rendered anhydrous by fusion, is known under the name of *patent yellow*, *Turner's yellow*, or *Cassel yellow*, $=PbCl+7PbO$. A similar compound may be obtained by fusing together 1 part of chloride with 4 or 5 of oxide of lead, or by heating salammoniac with oxide of lead.

IODIDE OF LEAD (PbI) may be formed by heating leaf-lead with iodine; but it is most readily obtained by adding iodide of potassium to a solution of nitrate of lead, in equivalent proportions; it then falls in the form of a bright yellow powder, soluble in about 1250 of cold and 200 parts of boiling water, and separates, as this solution cools, in brilliant flakes, which are hexahedral, or derivatives of the hexahedron. In this crystalline state it retains its color, but the pulverulent iodide becomes pale by exposure to light. When gently heated it becomes deeper colored, and even brown, but again yellow on cooling: at higher temperatures it fuses, and volatilizes at a strong red heat. It is soluble in aqueous solutions of potassa and soda, forming double salts: boiled with carbonate of potassa, it forms carbonate of lead and iodide of potassium. It becomes white when digested in caustic ammonia, forming the compound, $=NH_3,PbI$; the same compound is obtained by the action of gaseous ammonia upon the iodide. Iodide of lead is soluble in hydrochloric acid, and if concentrated by heat, the solution as it cools deposits radiated prismatic crystals of a yellow color, composed of iodide and chloride of lead. It dissolves in concentrated solutions of the alkaline iodides, and in the acetates of potassa, soda, and ammonia. An *iodide of lead and sodium* is thus formed by adding slight excess of iodide of sodium to a hot solution of iodide of lead, and placing the liquid in a warm place; it separates in yellow shining laminæ $=NaI,2PbI$. It forms a similar crystallizable double salt with iodide of potassium.

BROMIDE OF LEAD ($PbBr$) is precipitated from a solution of lead by hydrobromic acid or bromide of potassium: it is white, crystalline, fusible, and concretes on cooling into a yellow mass. It is sparingly soluble in water, and its boiling solution deposits shining acicular crystals.

FLUORIDE OF LEAD (PbF) is almost insoluble, and obtained by adding hydrofluoric acid to nitrate of lead, when it falls in the form of a white powder, soluble in nitric and hydrochloric acids.

SULPHIDE OF LEAD (PbS) may be formed by fusion: when the lead melts, it suddenly combines with the sulphur with ignition. Its lustre and color much resemble pure lead, but it is brittle, and requires a bright red heat for fusion. Its specific gravity is 7·58. Boiled with hydrochloric acid, chloride of lead and sulphuretted hydrogen are formed; by nitric acid it is converted into sulphate of lead. Sulphide of lead may be obtained in the humid way, by precipitating any salt of lead by sulphuretted hydrogen: the precipitate is black, or brown if the solution is dilute: this is so delicate a test of lead, that a solution containing a hundred-thousandth part of the metal is discolored by it, provided no excess of acid be present.

Native sulphide of lead, or *galena*, is the principal source of the commercial demands of the metal. It occurs massive, and crystallized in cubes and their modifications. When galena is finely powdered and heated with strong nitric acid, it is converted into sulphate of lead, the other metals associated with it (copper and silver) being dissolved as nitrates. When the nitric acid is diluted, some nitrate of lead is formed and dissolved, and a portion of sulphur is precipitated.

SULPHITE OF LEAD (PbO,SO_2) is formed by digesting protoxide of lead in aqueous sulphurous acid; or by adding the acid to nitrate of lead. It is white, insoluble in water, and tasteless.

SULPHATE OF LEAD (PbO,SO_3).—Cold sulphuric acid has no action upon metallic lead; but when boiled in the concentrated acid, sulphurous acid is evolved, and sulphate of lead formed. It is easily produced by adding dilute sulphuric acid, or a soluble sulphate, to a solution of nitrate of lead, when it falls in the form of a dense white powder: hence the application of the soluble salts of lead, especially the nitrate, as tests of the presence of sulphuric acid and sulphates. After having been dried at 400°, it may be heated to redness without losing weight. Heated on charcoal by the blowpipe, it is ultimately reduced. Sulphate of lead is insoluble in water and in alcohol. It is sparingly soluble in excess of sulphuric acid, and separates from it in small prismatic crystals. It is soluble, when recently precipitated, in hydrochloric acid, the fixed alkalies, and sparingly so in their carbonates, and in some of the salts of ammonia, especially the acetate. Its acid is expelled by the action of silica and of alumina at a red heat, hence its decomposition when fused in earthen crucibles. This compound is found native, crystallized in rhombs in Anglesea, Scotland, and other localities.

PHOSPHATE OF LEAD.—Each modification of phosphoric acid gives a white precipitate in the soluble salts of lead, which is soluble in nitric acid.—*Native phosphate of lead.* The mineral usually so called is a compound of phosphate and chloride of lead, in which 3 atoms of the tribasic phosphate are combined with 1 of chloride ($9PbO,3PO_5+PbCl$). It has been found in the mines of Cumberland, Durham, Yorkshire, and of Wanlock Head in Scotland, and in many of the foreign mines. Its color is various shades of green, yellow, and brown. It usually occurs in six-sided prisms, semitransparent and brittle.

CARBONATE OF LEAD. *Ceruse; White Lead.* (PbO,CO_2)—This important compound is extensively employed as an oil-pigment: it is chiefly made in London and at Newcastle-on-Tyne, to the annual quantity of about 16,000 tons. There are many processes by which it may be obtained, and much ingenuity has been displayed in their modification and improvement, the great objects being to obtain it in such a state that it shall form the most opaque and densest *body* as it is called, when ground up with linseed, or other drying oil, and shall at the same time be of a pure and perfect white.

The following is an outline of the several methods by which this carbonate may be formed. 1. By the precipitation of soluble salts of lead by alkaline carbonates. A solution of nitrate or acetate of lead is thus decomposed by carbonate of soda; it yields a dense white precipitate, which, when washed and dried, is of a pure white, but when examined by a magnifier, is found to consist of minute crystalline grains, a circumstance which interferes with its body or opacity to such an extent as to render it unfit for oil-paint: it is also a pure or neutral carbonate, and it will appear that the most esteemed *white lead* generally contains more or less oxide or hydrated oxide of lead. It varies in texture according as the carbonate is added to the nitrate, or the nitrate to the carbonate; the latter mode of precipitation, with properly diluted solutions, furnishes the most impalpable powder. When the carbonate has once acquired a crystalline texture, no grinding or mechanical comminution is capable of conferring upon it the qualities which fit it for an oil pigment. 2. When carbonic acid gas is passed through a hot solution of subnitrate of lead, carbonate of lead is thrown down, and the solution reverts to the state of neutral nitrate: this is reconverted into subnitrate by boiling with protoxide of lead (powdered litharge), and the precipitation continuously repeated. 3. Subacetate of lead is decomposed by passing through it a current of purified carbonic acid gas. The celebrated white lead of Clichy is thus prepared. 4. Finely powdered litharge is moistened, mixed with a very little acetate of lead (about a hundredth part), and submitted during constant stirring to a current of heated carbonic acid: in this process a subacetate of lead is successively formed and decomposed; a small quantity only of the original acetate therefore is required. 5. In the *Dutch process* lead is cast into plates or bars, or into the form of stars, or circular gratings of six or eight inches in diameter, and from a quarter to half an inch in thickness: five or six of these are placed one above another in the upper part of a conical earthen vessel, something like a garden-pot, in the bottom of which there is a little strong acetic acid. These pots are then arranged side by side, on the floor of an oblong brick chamber, and are imbedded in a mixture of new and spent tan (ground oak-bark as used in the tanyard). The first layer of pots is then covered with loose planks, and a second range of pots imbedded in tan is placed upon the former; and thus a stack is built up so as entirely to fill the chamber with alternate ranges of the pots containing the lead and acetic acid, surrounded by and imbedded in the tan. Several ranges of these stacks occupy each side of a covered building, each stack containing about 12,000 of the pots, and from 50 to 60 tons of lead. Soon after the stack is built up the tan gradually heats or ferments, and begins to exhale vapor, the temperature of the inner parts of the stack rising to 140° or 150°. The acetic acid is slowly volatilized, and its vapor passing readily through the gratings or folds of lead, gradually corrodes the surface of the metal, upon which a crust of subacetate is successively formed and converted into carbonate, there being an abundant supply of carbonic acid furnished by the slow fermentative decomposition of the tanners' bark. In the course of from 4 to 6 weeks the process is completed, and now, on unpacking the stacks, the lead is found to have undergone a remarkable change: the form of the castings is retained, but they are converted, with considerable increase of bulk, into carbonate of lead; this conversion is sometimes entire, at others it penetrates only to a certain depth, leaving a central skeleton of metallic lead, the conversion being unequal in different parts of the stack, and varying in its perfection at different seasons, temperatures, and states of the atmosphere. The stacks are so managed that they are successively being built up and unpacked. The corroded and converted gratings, or cakes, are then passed through rollers, by which the carbonate of lead (white lead) is crushed and broken up, and the central core of metallic lead (blue lead), if any remain, is easily separated: the white lead is then transferred to the mills, where it is ground up into a thin paste with water, and is ultimately reduced, by the process of elutriation, or successive washings and subsidences, to the state of an impalpable powder; it is then dried in wooden bowls placed upon shelves in a highly-heated stove, and thus brought to the state of masses easily rubbed between the fingers into a fine powder, in which the microscope does not enable us to discern the slightest traces of crystalline character. If intended for the use of the painter, it is next submitted to grinding with linseed oil; and it is found that a hundred weight of this white lead is formed into a proper consistence with 8 pounds of oil, whereas precipitated white lead requires 16 pounds of oil for the same purpose; the one covering the surface so much more perfectly, and having so much more body than the other. It is sometimes supposed that in this process the oxygen and carbonic acid required to form the carbonate of oxide of lead are derived from the decomposition of the acetic acid; but this is evidently not the case, for not more than 100 pounds of real acetic acid exist in the whole quantity of the dilute acid contained in the several pots of each stack; and in 100 pounds of acetic acid there are not more than 47 to 48 pounds of carbon, whereas 6740 pounds would be required to furnish the carbonic acid which should convert 50 tons of lead (the average weight of that metal in each stack) into carbonate of lead. There can be no doubt then that the carbon or carbonic acid must come from the tan, and that the oxygen is partly derived from the same source, and partly from the atmosphere: the principal action of the acetic acid, therefore, is to form successive portions of subacetate of lead, which are successively decomposed by the carbonic acid: the action is, however, of a very remarkable description, for even masses of lead, such as blocks of an inch or more in thickness, are thus gradually converted through and through into carbonate, so that if due time is allowed, there is no central remnant of metallic lead. The original texture of the lead is much concerned in the extent and rapidity of the conversion. Rolled or sheet lead will not answer, and the gratings, coils, and stars which are employed, are all of cast lead. The purest metal is also required; for if it contain iron, the resulting white lead acquires a tawny hue; and if a trace of silver, it acquires a perceptible dinginess when subjected to the action of light.

Sulphate of baryta is occasionally added to commercial white lead, by which its valuable properties are proportionately deteriorated; the adulteration is easily detected by digesting the sample in dilute nitric acid, which dissolves the carbonate of lead, but leaves the sulphate of baryta; the articles known under the name of *Venice white*, *Hamburgh white*, and *Dutch white*, are avowedly mixtures of sulphate of baryta with carbonate of lead. *Clichy white*, *Krems* or *Kremnitz white*, and *Silver white*, are pure white lead. A minute addition of indigo or of lamp-black is sometimes made to white lead, to give it a slight bluish shade.

Carbonate of lead is usually in the form of a heavy white powder, insoluble in water, and very sparingly soluble in aqueous carbonic acid; its specific gravity varies from 6·4 to 6·75. It entirely dissolves with effervescence in acetic and in dilute nitric acid. It is immediately discolored and ultimately blackened by sulphuretted hydrogen, whence the necessity of the cautious exclusion of all sources of that compound in white-lead works. When carefully heated in the contact of air carbonate of lead loses carbonic acid, and furnishes by proper management a beautiful *minium*.

The usual composition of commercial white lead, prepared by the Dutch process, is represented by Phillips (*Journ. Chem. Soc.* iv. 170) as $2(PbO, CO_2)+PbO,HO$. It loses the whole of its water at 300°, and at 350° the carbonic acid begins to be evolved.

Native Carbonate of Lead is one of the most beautiful of the metallic ores; it occurs crystallized, and fibrous, the former transparent, the latter generally opaque. It is soft and brittle, and occasionally tinged green with carbonate of copper, or gray by sulphide of lead.

CYANIDE OF LEAD ($PbCy$) falls in the form of an insoluble white powder when cyanide of potassium is added to a solution of nitrate of lead, or when hydrocyanic acid is dropped into acetate of lead: heated to redness in a glass tube, it gives out nitrogen, and leaves a pyrophoric *carbide of lead.*

BORATE OF LEAD is precipitated in the form of a white powder when borate of soda is mixed with nitrate or acetate of lead: it fuses into a colorless glass, and probably consists of 2 atoms of boracic acid and 1 of protoxide of lead. Boracic acid and oxide of lead may be fused together in all proportions; 112 of oxide and 24 of acid give a soft yellow glass, sp. gr. 6·4; with 48 of acid the glass is less yellow and harder; and with 72 of acid it is colorless, as hard as flint glass, and highly refractive.

ALLOYS OF LEAD.—With *tin*, lead forms several useful alloys, which are somewhat less dense than the mean. Common *pewter* consists of about 80 parts of tin and 20 of lead. Equal parts of lead and tin constitute *plumbers' solder*. When pieces of *copper* are thrown into red-hot melted lead, they soon disappear, and form a gray, brittle, and granular alloy. In coating *iron* with lead, the surface of the metal is first cleaned with hydrochlorate of ammonia: it is then dipped into melted zinc, and afterwards into a bath of melted lead.

TESTS FOR THE SALTS OF LEAD.—The salts are for the most part white, and those which are soluble form colorless solutions. They have a sweetish metallic taste. 1. *Sulphuretted hydrogen* gives a brownish discoloration even when less than 1-100,000th part of a salt of lead is present. In ordinary solutions, it throws down a brown-black precipitate (sulphide of lead), insoluble in alkalies and in diluted mineral acids, but decomposed by strong nitric acid. 2. *Hydrosulphate of ammonia* gives a similar precipitate, not soluble in an excess of the reagent, and having the other properties of the sulphide. The insoluble salts of lead, such as the sulphate and phosphate, are decomposed by this liquid, and a soluble salt of the acid is formed. 3. Diluted *sulphuric acid* throws down a white precipitate, slowly in acid solutions. This precipitate is soluble in potassa and strong hydrochloric acid. 4. *Potassa* and *soda* throw down a white precipitate, soluble in excess of the alkaline liquid. 5. *Ammonia* precipitates a white hydrated oxide, not soluble in an excess of the alkali. 6. All the alkaline *carbonates* throw down white precipitates, insoluble in an excess. 7. *Iodide of potassium* gives a yellow precipitate, soluble in potassa and in hydrochloric acid. 8. *Chloride of sodium* gives a white precipitate, partly dissolved when boiled, and readily dissolved by potassa or strong nitric acid. The lead-precipitates dissolved by alkalies are thrown down black by sulphuretted hydrogen or hydrosulphate of ammonia. 9. *Ferrocyanide of potassium* gives a white precipitate.

The *salts insoluble in water* are dissolved by soda and potassa, or by nitric acid, when the metal is rendered manifest by sulphuretted hydrogen and other tests. When these salts are boiled with carbonate of soda, they afford carbonate of lead, which may be dissolved in acetic or dilute nitric acid, and subjected to the usual tests. Heated by the blowpipe upon charcoal, with carbonate of soda or cyanide of potassium, they afford a globule of metal. Lead is precipitated from its solutions, in the metallic state, by zinc. All the soluble, as well as the difficultly-soluble, salts of lead may be decomposed and reduced, by mixing them with dilute nitric or hydrochloric acid, and immersing a plate of zinc in the liquid.

When solutions of the salts of lead are filtered through charcoal, which is sometimes done for the purpose of decoloration, part or even the whole of the oxide of lead, if it only amount to about one-twentieth of the charcoal employed, will be abstracted by the charcoal. This renders charcoal in coarse powder most useful in the construction of the filters for domestic purposes. Any casual impregnation of water by lead may thus be removed, and the water rendered wholesome. So small a quantity as one grain of lead in a gallon of water has been known to produce the effects of lead-poisoning.

CHAPTER XXXIII.

BISMUTH—COBALT—NICKEL—CHROMIUM.

BISMUTH ($Bi=213$).

THIS metal was first described by Agricola, in 1529. It is sometimes called *marcasite.* It is neither of common occurrence, nor very abundant. *Native bismuth* is found in Cornwall, and in Saxony, Transylvania, and Bohemia. It is readily extracted from its ores by fusion. Bismuth is a brittle white metal, with a slight tint of red. It fuses at 507°, and expands and crystallizes on cooling. Its sp. gr. is 9·8. To obtain fine crystals, it should be purified by fusion with nitre, and when thus refined, carefully melted and poured into a heated mould, and suffered slowly and quietly to cool. When the surface has solidified, the crust is pierced, and the liquid metal poured out from the interior: the mould is then suffered to cool, and the superior crust carefully removed, when the cavity is found lined with iridescent cubical crystals (pp. 25 and 291). Arsenic, iron, copper, nickel, silver, and other metals, are frequently found in the bismuth of commerce. To purify it, it may be dissolved in nitric acid, and the clear solution poured off into water, which occasions a precipitation of a subnitrate of bismuth, easily reducible by fusion with charcoal or black flux in an earthen crucible.

BISMUTH AND OXYGEN.—There are two well-defined oxides of bismuth, a teroxide$=BiO_3$, and an acid oxide$=BiO_5$. A third oxide has been described as a compound of these$=BiO_3,BiO_5$.

OXIDE OF BISMUTH; TEROXIDE OF BISMUTH (BiO_3). When bismuth is exposed at a white heat to a current of air, it burns, and produces an abundant yellow smoke, which condenses in the form of a yellowish-white sublimate. The readiest mode of obtaining this oxide consists in dissolving bismuth in nitric acid, precipitating by dilution with water, edulcorating the precipitate, and heating it, when dry, nearly to redness. Owing to imperfect washing, it frequently contains traces of arsenic acid. At a red heat, this oxide fuses, and when in fusion it acts upon other oxides much in the same way as oxide of lead. It forms, on cooling, a yellow vitreous mass of a specific gravity of 8·2. It is easily reduced by hydrogen, charcoal, and several of the metals. It combines with water, forming a white *hydrate,* which is best obtained by digesting the precipitate formed by pouring the nitric solution of bismuth in water, into caustic potassa or soda, and after washing, drying it at 80°. It is insoluble in excess of the alkalies (and their carbonates); and when boiled with them becomes yellow and anhydrous. It is also insoluble in tartaric acid, by which it is known from the antimonial precipitate in water. *Native oxide of bismuth* is a rare mineral, found in Cornwall and Saxony: it is the *bismuth ochre* of some mineralogists.

PEROXIDE OF BISMUTH; *Bismuthic Acid* (BiO_5).—This oxide is obtained by dropping nitrate of bismuth into a solution of caustic potassa, boiling in the alkaline liquor, washing the precipitate, and, whilst moist, diffusing it through a solution of potassa into which chlorine is passed; a red precipitate is thus formed, which consists of bismuthic acid and teroxide, and which is to be digested in nitric acid of sufficient strength to dissolve the oxide. The remaining acid, which is a hydrate, is to be well washed, and dried at 100°; it is a red powder, becoming brown and anhydrous when dried at 266°; at higher temperatures it begins to lose oxygen. It is decomposed by sulphuric acid, and by hot nitric acid.

NITRATE OF BISMUTH ($BiO_3,3NO_5,9HO$).—When nitric acid is poured upon powdered bismuth, the action is intensely violent. Nitrate of bismuth is usually made by dissolving the metal to saturation in 2 parts of nitric acid and 1 of water; nitric oxide is copiously evolved, and the solution affords prismatic crystals, which may be dissolved in a small quantity of water; but if the solution, even when acid, is poured into a large quantity of water, it is decomposed, and affords a white and somewhat crystalline precipitate, commonly called *subnitrate of bismuth*, and formerly known as *magistery of bismuth, pearl white*, and *blanc d'Espagne;* it is insoluble in water, and when dried in the air is $=BiO_3,NO_5,HO$; but becomes anhydrous when adequately dried. This compound is used in medicine: it frequently contains arsenic in the form of arsenic acid, owing to imperfect washing of the precipitate. Out of five druggist's samples, we have found arsenic in three. The presence of this impurity may lead to a serious error.

The nitrate is not so completely decomposed by water as the chloride: hence, in order to procure the complete decomposition of the nitrate, some hydrochloric acid should be added to the solution, and this should be afterwards concentrated by evaporation. The addition of a large quantity of water to the residue will then produce a copious white precipitate. (*See* CHLORIDE.)

CHLORIDE OF BISMUTH; *Terchloride.* ($BiCl_3$) is procured by gently heating the metal in chlorine; it burns, and forms a gray compound. This terchloride may also be prepared by heating 2 parts of corrosive sublimate with 1 of powdered bismuth, and expelling the excess of the former by heat; or by evaporating the solution of oxide of bismuth in hydrochloric acid to dryness, and heating the residue in close vessels. It was formerly called *Butter of Bismuth.* It is of a gray color, and fuses at about 480°. When exposed to air it deliquesces. It is decomposed by a large quantity of water.

A solution of this compound may be obtained by dissolving pure teroxide of bismuth, or the pure sulphide, in hydrochloric acid, and evaporating the liquid. When added to a large quantity of water, a white oxychloride of the metal is precipitated ($3BiCl_3+6HO=BiCl_3,2BiO_3+6HCl$). A small quantity of oxide of bismuth is, however, retained by the acid liquid. This precipitate has also received the name of *pearl white.*

SULPHIDE OF BISMUTH (BiS_3) is of a bluish and metallic lustre; it is less fusible than bismuth. It may be formed by fusion; and also by precipitating the salts of bismuth by sulphuretted hydrogen, when it forms a black or dark-brown precipitate (hydrated), which, when dried and heated, acquires a metallic lustre.

SULPHATE OF BISMUTH ($BiO_3,3SO_3$) is obtained by heating powdered bismuth in sulphuric acid. It is a white compound, insoluble in, but decomposed by water, which converts it into a subsulphate and supersulphate.

CARBONATE OF BISMUTH is thrown down from the nitrate by carbonated alkalies; it is a white powder, insoluble in water and in carbonic acid, and soluble in nitric acid with effervescence.

ALLOYS OF BISMUTH.—Those with *tin* and *lead* are remarkable for the low temperature at which they enter into fusion, and for the extraordinary irregularities of expansion and contraction which they exhibit with changes of temperature. An alloy of 2 parts of bismuth, 1 of lead, and 1 of tin, fuses at 200°. The alloy of 8 parts of bismuth, 5 of lead, and 3 of tin, fuses at a little below 212°: the addition of 1 part of mercury or of cadmium renders it still more fusible. It may be employed for taking casts from medals, and even from the surface of wood and embossed paper: some beautiful casts have also been made, in this alloy, of the internal ear, showing the complexities of its bony cavities. When the alloy is poured upon a marble slab, and broken as soon as it is cool enough to be handled, its surfaces are bright and conchoidal, and the whole extremely brittle; after this it becomes hot, and loses its brittleness, its fractured surface becoming granular and dull.

TESTS FOR THE SALTS OF BISMUTH.—Many of them are resolved by water into a soluble acid salt, and a less soluble or insoluble and more basic compound. 1. In the clear acid solutions of oxide of bismuth, potassa, soda, and ammonia, and their carbonates, produce white precipitates, insoluble in excess of the alkali, or its carbonate, and insoluble in hydrochlorate of ammonia. 2. Hydrosulphate of ammonia and sulphuretted hydrogen produce brown or black precipitates, insoluble in the precipitants, but soluble in boiling nitric acid, and easily reduced to metallic bismuth when mixed with soda, and fused in the inner flame of the blowpipe. 3. Chromate of potassa gives a golden-yellow precipitate, soluble in nitric acid, but insoluble in potassa. 4. Iodide of potassium gives a purple-brown precipitate. 5. Sulphuric acid does not precipitate the solution; and by this reagent lead may be detected in, and separated from, bismuth. 6. Ferrocyanide of potassium gives a greenish-white precipitate, and ferricyanide a similar precipitate, but of a deeper color. 7. The acid solutions of bismuth are decomposed by zinc, lead, tin, and cadmium. A piece of zinc introduced into the solution is soon covered with a black uncrystalline deposit of reduced bismuth, which protects it from the further action of the acid. All the compounds of bismuth give a metallic button on charcoal under the blowpipe flame. The metal is surrounded with a yellow border of anhydrous oxide.

Bismuth may be mistaken for antimony from the fact that its salts, especially the chloride, produce white precipitates when added to a large quantity of water, provided too much of the acid is not present. The white precipitate from bismuth is not soluble in tartaric acid, and is blackened by sulphuretted hydrogen; that from antimony is easily dissolved by tartaric acid, and acquires a deep orange-red color from the gas.

COBALT ($Co=30$).

The *native* combinations of cobalt are the oxide, and compounds of the metal with iron, nickel, arsenic, and sulphur. The ore called *glance cobalt* is a sulpho-arsenide. The *red ore* is an arseniate.

Cobalt is never employed in the metallic state, so that the processes for its reduction are generally carried on upon a small scale, and confined to the experimental laboratory; but there is much difficulty in obtaining it pure. It is a metal of a reddish-gray color, brittle, and difficultly fusible. Its sp. gr. is 8·9. It forms two oxides, a *protoxide* and a *sesquioxide*, and these combine with each other.

PROTOXIDE OF COBALT (CoO), formed by adding potassa to the nitrate and washing and drying the precipitate out of contact of air, appears nearly black. By exposure to heat and air it absorbs oxygen, and is converted into peroxide. The protoxide, when recently precipitated and moist, is *blue;* if left in contact of water, it becomes a *red hydrate;* it then absorbs oxygen, and acquires a green tint. It may also be obtained by heating the carbonate of cobalt out of contact of air; it is then of a greenish-gray color. It is recognized by the facility with which it imparts a blue tint to vitrifiable compounds, and to white enamel. When hydrogen is passed over it at a red heat, it is decomposed, and porous metallic cobalt remains, which is sometimes pyrophoric.

PEROXIDE OF COBALT; *Sesquioxide of Cobalt* (Co_2O_3.)—When the protoxide is heated in the air, it absorbs oxygen, and acquires a dark-brown color, forming an oxide intermediate between the peroxide and protoxide, = Co_3O_4. When chlorine is passed through a mixture of the hydrated protoxide and water, or when a solution of chloride of cobalt is decomposed by chloride of lime, a black precipitate falls, which is the *hydrated peroxide* (Co_2O_3,3HO), and which may be deprived of water by cautious drying; it is then black, and insoluble in dilute acids; it does not form salts; when acted on by hydrochloric acid it evolves chlorine, and yields a protochloride.

NITRATE OF COBALT (CoO,NO_5).—With nitric acid the oxide of cobalt furnishes a brownish-red deliquescent salt, in rhombic crystals, consisting of CoO,NO_5,6HO. Characters written with it upon paper become pink in dry air, and disappear in a damp atmosphere. It thus forms a red sympathetic ink.

CHLORIDE OF COBALT (CoCl).—When oxide of cobalt is dissolved in hydrochloric acid, evaporated to dryness, and the residuum heated to redness out of the contact of air, a substance of a blue color and micaceous texture is obtained, which is anhydrous chloride of cobalt. When this chloride is dissolved in water, it yields a pink solution, which, if written with, becomes invisible when dry; but if gently heated, the writing appears in brilliant blue (anhydrous chloride), which soon vanishes as the paper cools, in consequence of the salt absorbing aërial moisture (hydrochlorate of the oxide, p. 70); if overheated, the writing blackens. This solution has been termed *sympathetic ink*. When evaporated, it forms red crystals, composed of 1 atom of the chloride and 5 of water.

PROTOSULPHIDE OF COBALT (CoS) is yellowish-gray; it fuses at a red-heat, and is easily soluble in acids.

SESQUISULPHIDE OF COBALT (Co_2S_3) is obtained by decomposing sulphate of cobalt by sulphuretted hydrogen at a red heat. It is dark gray, and occurs *native*.

SULPHATE OF COBALT (CoO,SO_3) forms oblique rhombic prisms, soluble in 24 parts of water at 60°, and insoluble in alcohol. It may be made by dissolving the newly-precipitated protoxide or carbonate of cobalt in sulphuric acid diluted with its bulk of water. When dried at a temperature of 500° the crystals fall into a blue powder, which in a red heat fuses, but does not give off acid except at a very high temperature. When 1 part of sulphate of cobalt and 2 or 3 of sulphate of zinc are dissolved together and precipitated by carbonate of soda, a precipitate falls which, when washed and calcined, has been used as a pigment, under the name of *Rinmann's green*.

PHOSPHATE OF COBALT (3CoO,PO_5) may be formed by adding phosphate of soda to chloride of cobalt; it is insoluble in water, of a lilac color, and soluble in excess of phosphoric acid.—*Thénard's Blue.* When phosphate of cobalt is mixed with pure and moist alumina, and exposed to heat, it produces a blue compound, which has been employed as a substitute for ultramarine. A pure salt of cobalt free from nickel, and pure alumina free from iron, are essential to the production of a fine blue.

CARBONATE OF COBALT.—When nitrate, chloride, or sulphate of cobalt, is decomposed by carbonate of soda, a purple powder is precipitated, becoming pink when dried, and soluble with effervescence in the acids. Heated in close vessels it gives off carbonic acid, and a gray protoxide remains: it is a mixture of carbonate and hydrated oxide = 5CoO,$2CO_2$,4HO.

AMMONIA COMPOUNDS OF COBALT.—Several of the salts of cobalt form double salts with those of ammonia.

When hydrated oxide of cobalt is dissolved in an ammoniacal solution of sal-ammoniac, it absorbs oxygen from the air, and acquires a purple color; and if excess of hydrochloric acid be then added, and the mixture boiled, a crimson precipitate falls, leaving the liquor colorless. When this precipitate is dissolved in hot water, acidulated by hydrochloric acid, it deposits red octahedral crystals, insoluble in hydrochloric acid, and which, at a red heat, lose ammonia, and hydrochlorate of ammonia: their composition is $3(NH_4Cl+2(CO)NH_2)$.

COBALTOCYANIDES.—When cyanide of potassium is added to a solution of cobalt salt, a brown precipitate (CoCy) falls, which, dissolved in an excess of cyanide of potassium, yields a double cyanide=KCy,CoCy. When this salt is exposed to the air, or when a solution of hydrated oxide of cobalt in potassa is supersaturated with hydrocyanic acid, a salt is formed$=K_3,Co_2,Cy_6$. It corresponds to the ferricyanide of potassium. Similar salts, with sodium and other bases, have been obtained.

BORATE OF COBALT.—Solution of borax occasions a pink precipitate in solution of chloride of cobalt, which is a *borate of cobalt*, and which produces a beautiful blue glass when fused.

USES OF COBALT.—The chief use of cobalt is in the state of *oxide* as a coloring material for porcelain, earthenware, and glass: it is principally imported from Germany in the state of *zaffre*, and *smalt*, or *azure*. *Zaffre* is prepared by calcining the ores of cobalt, by which sulphur and arsenic are volatilized, and an impure oxide of cobalt remains, which is mixed with about twice its weight of finely-powdered flint. *Smalt* and *azure blue* are made by fusing zaffre with glass, or by calcining a mixture of equal parts of roasted cobalt ore, common potassa, and ground flint. In this way a blue glass is formed, which, while hot, is dropped into water, and afterwards reduced to impalpable powder. Thénard's blue is a valuable pigment, and has been substituted for smalt in the manufacture of paper, though it is said not to be so effectual in covering the yellow tint of the paper. There was formerly a large addition of smalt made to bank-note paper, and consequently the ash obtained by the periodical combustion of notes at the Bank, often assumed by fusion the appearance of a deep blue glass: so also the blue-tinted writing-papers leave a fine blue ash when burned, and often exhale an aliaceous odor from the presence of arsenic in the smalt. Smalt generally contains traces of arsenic, and this substance may be thus transferred to starch and paper. In paper-making, there is some difficulty in keeping the smalt uniformly suspended in the pulp, so that the under side of the sheet is generally bluer than the upper. The manufacturers of paper-hangings also use smalt and Thénard's blue for all brilliant and durable blues.

TESTS FOR THE SALTS OF COBALT.—The salts are generally blue in the anhydrous state, as well as in concentrated acid solutions. If diluted, they have a crimson or pink-red color. 1. *Sulphuretted hydrogen* does not precipitate an acid solution. If acetate of soda is added to the liquid, a dark-brown precipitate (CoS) falls. 2. *Hydrosulphate of ammonia* produces a dark-brown or black precipitate, which is quite insoluble in an excess of the reagent. 3. *Ammonia* gives a bluish precipitate, soluble in an excess of the alkali: the precipitate, on exposure to air, rapidly acquires a green, and finally a brown color. 4. *Potassa* throws down a deep blue precipitate, which, when boiled without exposure to air, becomes rose-red. The blue precipitate exposed to air becomes olive-green, and finally brown. 5. *Alkaline carbonates* give a light-red precipitate of basic carbonate. This precipitate is dissolved by carbonate or hydrochlorate of ammonia, forming a rich crimson-red solution. 6. *Ferrocyanide of potassium* produces a deep green, and *Ferricyanide of potassium*, a red-brown colored precipitate.

The salts of cobalt which are insoluble in water are dissolved by hydrochloric and sulphuric acids. The hydrochloric solution on paper is identified by the red spot or streak acquiring a rich blue color when dried by a moderate heat, and by its resuming the ordinary red color when exposed to damp air (p. 70). Before the blowpipe, borax and microcosmic salt acquire a blue color from cobalt and the compounds containing it.

NICKEL ($Ni=30$).

Nickel was discovered by Cronstedt, in 1751. Its commonest ore was termed by the German miners, *kupfernickel*, or "false-copper:" it is an arsenide of nickel. The common commercial source of nickel is an impure fused arsenide known under the name of *Speiss;* it generally contains between 50 and 60 per cent. of nickel. The pure metal may be obtained from this arsenide by roasting it, dissolving the product in a mixture of equal parts of nitric and hydrochloric acids, and evaporating the solution to dryness, so as to expel excess of acid; then redissolving the residue in water, passing a current of sulphuretted hydrogen through the solution, and filtering. A little nitric acid is added to the filtrate, and after boiling it, an excess of caustic ammonia is added; it is again filtered, and solution of potassa added until the blue color of the liquid nearly disappears; this produces a green precipitate, which, when thoroughly washed with boiling distilled water, dried, and exposed to a red heat in a current of hydrogen gas, leaves the nickel in a finely divided state. It may be obtained in the form of a button by fusion at a white heat.

Nickel is a white, ductile, and malleable metal, nearly as difficult of fusion as iron: it is magnetic, but its magnetism is more feeble than that of iron, and vanishes at a heat somewhat below redness. It is not oxidized at common temperatures, but when heated it acquires various tints, like steel, and at a red heat becomes coated by a gray oxide. Its sp. gr. is 8·8. It is slowly soluble in dilute sulphuric and hydrochloric acids, evolving hydrogen, and producing protosalts: nitric acid is its best solvent.

PROTOXIDE OF NICKEL (NiO) is obtained by adding potassa to the solution of the nitrate or sulphate; a green precipitate falls, which is a *hydrated protoxide;* this, heated to redness, affords a gray protoxide. The carbonate, oxalate, and nitrate of nickel, when heated to redness, also afford the protoxide in the form of a gray powder: when intensely heated out of contact of air, the oxide becomes green. It is not magnetic. This oxide, in the state of hydrate, dissolves in ammonia, forming a sapphire-blue solution, a property made use of to separate oxides of nickel and iron, the latter (peroxide) being insoluble in ammonia.

PEROXIDE OF NICKEL; SESQUIOXIDE OF NICKEL (Ni_2O_3).—When nitrate or carbonate of nickel is carefully heated nearly to redness, a black powder remains, which is this oxide. It may be obtained as a *hydrate* by passing chlorine through the hydrated protoxide diffused in water, in which case a solution of protochloride is obtained, and peroxide is formed ($3NiO+Cl=NiCl+Ni_2O_3$). It may also be formed by the action of a warm solution of chloride of lime upon the hydrated protoxide. When this hydrated oxide is carefully dried, it is $=Ni_2O_3,3HO$. It does not combine with acids.

CHLORIDE OF NICKEL ($NiCl$).—When finely-divided nickel is heated in chlorine, it burns, and a golden-colored chloride results. This compound may also be obtained by dissolving the oxide in hydrochloric acid, evaporating to dryness, and heating the residue to redness in a glass tube: it then remains in the form of a yellow lamellar substance, volatile at a high red heat, which dissolves in hot water, and leaves on evaporation a confusedly crystalline mass of an apple-green color, and sweetish taste $=NiCl,9HO$.—*Ammonio-chloride of Nickel.* 100 parts of anhydrous chloride of nickel absorb 74·8 of ammonia, becoming a bulky white powder$=3(NH_3),NiCl'$ which yields a blue solution with water.

Nitrate of Nickel ($NiO,NO_5,5HO$).—Nitric acid acts upon nickel with disengagement of nitric oxide, and a bright green solution of protoxide is obtained, which yields prismatic crystals: exposed to heat, part of the acid may be driven off so as to leave a green insoluble subnitrate, and this at a higher temperature is decomposed, peroxide, or ultimately protoxide, of nickel remaining. The crystals of nitrate of nickel effloresce in dry air, but deliquesce in a damp atmosphere; they are soluble in 2 parts of water at 60°, and also in alcohol.

Sulphide of Nickel (NiS) may be formed by heating nickel filings with sulphur; they combine with ignition; also by heating oxide of nickel with sulphur; or by passing sulphuretted hydrogen over the heated oxide. It is yellow, and resembles pyrites.

Sulphate of Nickel ($NiO,SO_3,7HO$) is formed by dissolving the oxide or carbonate of nickel in diluted sulphuric acid: it yields emerald-green prismatic crystals, soluble in about 3 parts of water at 60°, and efflorescent by exposure; its taste is sweet and astringent; it is insoluble in alcohol and in ether. Exposed to heat, the crystals crumble down into a yellow powder: at a white heat the acid is expelled, and protoxide remains. When the ordinary crystals (containing 7 atoms of water) are exposed to the sunshine, or when long kept, they become a congeries of small octahedral crystals, which are opaque, but retain the original quantity of combined water.

Sulphate of Ammonia and Nickel.—($NH_4O,NiO,2SO_3,5HO$) is obtained by evaporating a mixed solution of sulphate of ammonia and sulphate of nickel; it forms four-sided prismatic crystals, of a blue-green color, soluble in four parts of cold water. Anhydrous sulphate of nickel absorbs gaseous ammonia, evolving heat, and forming a bulky pale blue powder, which gives a blue solution in water, and deposits green hydrated oxide: the amount of ammonia absorbed is about 56 per cent., so that the compound may be represented as $3(NH_3,)NiO,SO_3$. *Sulphate of Potassa and Nickel* ($KO,NiO,2SO_3,6HO$) is obtained by evaporating the mixed solution of sulphate of nickel and sulphate of potassa. It forms pale green rhomboidal crystals, isomorphous with the corresponding magnesian salt. Double sulphates of nickel and iron, and of nickel and zinc, may also be obtained.

Phosphate of Nickel, $3(NiO)PO_5$, being nearly insoluble, is precipitated upon adding phosphate of soda to a solution of nickel. It is of a pale-green color, and sometimes forms a crystalline powder.

Carbide of Nickel occasionally remains in the form of a shining powder, when a button of the metal which has been fused for a long time in contact with carbon is dissolved in nitric acid.

Carbonate of Nickel (NiO,CO_2) falls as a crystalline powder when a solution of nitrate of nickel is dropped into a solution of bicarbonate of soda. There is also a basic carbonate.

Cyanide of Nickel ($NiCy$) is thrown down as a green precipitate when a soluble cyanide is added to a solution of nickel, or when hydrocyanic is mixed with acetate of nickel.

Potassio-cyanide of Nickel ($KCy,NiCy$).—When freshly precipitated cyanide of nickel is dissolved in a solution of cyanide of potassium, yellow rhombic prisms are obtained on evaporation, which are this double cyanide with 1 atom of water. Similarly constituted salts may be obtained with the cyanides of ammonium, calcium, and barium.

Alloys of Nickel.—An alloy of nickel and *iron* forms a principal metallic ingredient in most *aërolites* or *meteoric stones*, and in the masses of native iron found in various parts of the world, in which the proportion of nickel varies from 1·5 to 8·5 per cent. With *copper*, nickel forms a hard white alloy. The *white copper* of the Chinese, or *Pakfong*, consists of 40·4 parts of copper, 31·6 of nickel, 25·4 of zinc, and 2·6 of iron. A similar alloy is often used as a substitute for silver, or for plated articles, under the name of *German silver;* it should consist of 8 parts of copper, 3 to 4 of nickel, and 3½ of zinc. A variety of articles are now plated with nickel by electrolytic precipitation from a solution of sulphate of nickel, the process being similar to that in which copper is used.

TESTS FOR THE SALTS OF NICKEL.—The salts of nickel are green in the hydrated, and yellow in the anhydrous state. Their solutions have a green color and an acid reaction. 1. *Sulphuretted hydrogen* produces no precipitate in an acid solution ; but if acetate of soda is added to the liquid in small quantity ; there is a dark-brown or black precipitate. 2. *Hydrosulphate of ammonia* gives a similar precipitate, which is only partially dissolved by an excess of the reagent. 3. *Ammonia* gives, in neutral solutions, a pale greenish precipitate, which is dissolved by an excess of the alkali, forming a blue solution. The precipitate is also soluble in hydrochlorate of ammonia. 4. *Potassa* gives a pale green precipitate of hydrated protoxide, insoluble in an excess of the alkali, but dissolved by hydrochlorate of ammonia. Potassa in excess gives a pale green precipitate in the blue solution formed by ammonia with a salt of nickel (3). The blue solution of a salt of copper in ammonia is not affected by the addition of potassa. 5. *Alkaline carbonates* give a similar precipitate soluble in an excess of carbonate of ammonia, forming a blue solution. 6. *Ferrocyanide of potassium* give a pale greenish precipitate even in the ammoniacal solution of nickel. This test forms a clear distinction between nickel and copper. The *Ferricyanide* gives a greenish-yellow precipitate. Before the blowpipe, these salts give with borax a reddish-yellow bead, which becomes paler as it cools, and which, in the reducing flame, yields grayish particles of reduced nickel.

CHROMIUM (Cr=26).

Chromium was discovered by Vauquelin in 1797. Its two native combinations are the *chromate of lead*, and the *chromite of iron*, a compound of the oxides of chromium and iron.

Metallic chromium may be obtained by intensely igniting its *oxide* with about a tenth of its weight of charcoal, but the reduction is difficult and imperfect. Its color resembles that of platinum ; it scratches glass, and takes a good polish. Its sp. gr. is 5·9. It has also been obtained by the action of potassium on chloride of chromium, and is then pulverulent, burns when heated, into an oxide, and is energetically acted on by most of the acids; whereas, when obtained by the usual modes of reduction, it is comparatively indifferent to the action of powerful reagents.

CHROMIUM AND OXYGEN.—There are four oxides of chromium—namely, *protoxide*, CrO; a sesquioxide, Cr_2O_3; an intermediate oxide, CrO,Cr_2O_3; and lastly, chromic acid, CrO_3. In addition to these, a perchromic acid has been announced, having the formula Cr_2O_7.

PROTOXIDE OF CHROMIUM (CrO) is obtained in the form of a brown hydrate, by the action of potassa on the corresponding *protochloride:* it is unstable, and passes by the action of air or water into the intermediate oxide, which is isomorphous with the magnetic oxide of iron.

SESQUIOXIDE OF CHROMIUM (Cr_2O_3) is obtained by heating chromate of mercury, or chromate of ammonia, to dull redness; it is also formed by the action of a red heat upon bichromate of potassa : in this case neutral chromate of potassa is formed, which may be removed by washing the product. This oxide is of a green color, and not changed by heat, and is much used in enamel and porcelain painting; it also forms an ingredient in the pink color of common earthenware, which is prepared by heating a mixture of 1 part of chromate of potassa with 30 of peroxide of tin, and 10 of chalk, to a red heat, and then washing the finely powdered product with dilute hydrochloric acid.

In its *hydrated* state this oxide is obtained by precipitation from its acid solutions: for this purpose a solution of bichromate of potassa may be strongly acidulated with sulphuric or hydrochloric acid, and boiled with the addition of a little alcohol, by which the red salt is deoxidized, and a green solution obtained, from which ammonia throws down a bulky greenish precipitate, which, when washed and dried in the air, is $Cr_2O_3,10HO$. When this hydrate has been heated, it shrinks, and is difficultly soluble. At a temperature a little below a red heat it suddenly becomes incandescent. It is a weak base, and forms green and purple solutions; the former do not crystallize, but the latter readily yield crystallizable salts.

Native Sesquioxide of Chromium has been found in the form of a green incrustation. It is the coloring matter of the emerald, and exists in a few other minerals, such as a diallage and some varieties of serpentine.

CHROMIC ACID (CrO_3).—This acid is most readily obtained by mixing 4 measures of a cold saturated solution of bichromate of potassa with 5 of sulphuric acid: the chromic acid separates, as the liquid cools, in crimson needles, which may be dried upon a porous tile, under a bell-glass. The crystals are very soluble in water, but sparingly soluble in sulphuric acid of the specific gravity of 1·55: they are anhydrous, and become of a very dark color when heated, but resume their scarlet tint on cooling; they fuse at about 400°, and when more highly heated become incandescent, giving off oxygen, and yielding sesquioxide. They taste sour and metallic. Chromic acid dissolves in alcohol, and the solution gradually deposits green oxide. It is a powerful oxidizing and bleaching agent, yielding half its oxygen to oxidizable bodies, and being reduced to sesquioxide; ($2CrO_3 = Cr_2O_3 + O_3$): hence a mixture of bichromate of potassa and sulphuric acid is frequently resorted to as a means of oxidizing organic bodies. It decomposes a solution of iodide of potassium, and sets free iodine, producing the usual blue color when starch is added to the mixture.

PERCHROMIC ACID (Cr_2O_7).—When chromic acid is agitated with peroxide of hydrogen, the liquid acquires a beautiful blue color (pp. 107, 140); and by means of ether, the blue-colored compound may be separated from the watery solution. It has not been obtained in an isolated state, or in combination with bases, but it is supposed to be chromic acid in a higher stage of oxidation; and its formula is assumed to be similar to that of the permanganic acid.

CHROMATE OF POTASSA (KO,CrO_3) is prepared by exposing a mixture of 4 parts of powdered native chromite of iron with 1 of nitre, to a strong heat for some hours, and washing out the resulting soluble matter: The process is repeated until the ore is decomposed. The washings yield *chromate of potassa* by evaporation.

This process is now generally conducted so as to yield a *bichromate*, by heating the pulverized chrome-iron ore with carbonate of potassa and a little nitre in a reverberatory furnace, and constantly stirring the mixture, to complete the oxidization: the product is then digested in water, and the yellow solution is supersaturated by nitric acid, which throws down silica, and by abstracting a portion of potassa leaves *bichromate*. Chromate of potassa forms yellow prismatic crystals of a disagreeable metallic taste, soluble in about twice its weight of water, and insoluble in alcohol. When heated to 400° it acquires a crimson color, but becomes again yellow on cooling. When fused it crystallizes on cooling, but is not decomposed except in contact of carbonaceous matter, when carbonate of potassa and oxide of chromium are produced.

BICHROMATE OF POTASSA ($KO,2CrO_3$) is obtained by adding a sufficiency of sulphuric or other acid to a solution of the chromate to give it a sour taste, and setting it aside for a day or two, when deep orange-colored or red crystals are deposited; the acid abstracts half the potassa, and if sulphuric acid is used, there is some difficulty in separating the sulphate from the chromate; nitric acid is preferable. The crystals are anhydrous prisms, permanent in the air, of a metallic taste, soluble in 10 parts of water at 60°, and much more soluble in boiling water. At a red heat they fuse into a transparent liquid, which congeals into a crystalline mass on cooling, and then falls to powder. At a white heat, half the acid of the salt is decomposed, forming a mixture of oxide of chromium and neutral chromate of potassa. When 3 parts of bichromate of potassa are gently heated with 4 of sulphuric acid, potassio-sulphate of chromium is formed, and oxygen evolved: $(KO,2CrO_3+4(SO_3,HO)=[KO,SO_3+Cr_2O_3,3SO_3]+4HO+3O)$. Both the chromate and bichromate have a deleterious action on the system when their solutions are brought much in contact with the skin, causing sores which are difficult to heal. Paper impregnated with these salts has photographic properties, and, when dried, forms excellent tinder. The solutions have powerful antiseptic properties.

BICHROMATE OF CHLORIDE OF POTASSIUM ($KCl,2CrO_3$).—When 2 atoms of chromic acid and 1 of chloride of potassium are dissolved in hydrochloric acid, crystals of this salt may be obtained in the form of flat prisms, having the color of the bichromate. This salt is permanent in the air, and may be dissolved without decomposition in dilute hydrochloric acid; but by pure water it is resolved into hydrochloric acid and bichromate. Similar bichromates of the chlorides of sodium, calcium, magnesium, and ammonium have been formed.

CHROMATE OF SODA (NaO,CrO_3) crystallizes in oblique rhombic prisms of a fine yellow color, very soluble in water, and sparingly so in alcohol.

BICHROMATE OF SODA ($NaO,2CrO_3$) is more soluble than the preceding: it forms prismatic and tabular crystals.

CHROMATE OF LEAD (PbO,CrO_3).—When chromate of potassa is added to any of the soluble salts of lead, a fine yellow powder falls, which is the neutral chromate: it is insoluble in water, but soluble in nitric acid, and in solution of potassa: solution of carbonate of potassa forms with it carbonate of lead and chromate of potassa. It is decomposed by sulphuric acid, sulphate of lead is formed, and chromic acid set free.

Native Chromate of Lead is of a deep orange-red color; it occurs crystallized in prisms, somewhat translucent and brittle. Specific gravity, 6.

DICHROMATE OF LEAD; SUBCHROMATE OF LEAD, $2(PbO),CrO_3$, is formed by digesting the neutral chromate in a dilute solution of caustic potassa; it is of a scarlet color. These chromates of lead are valuable pigments, and used both as oil and water colors, and in calico-printing and dyeing.

The mineral called *Vauquelinite* is a double chromate of lead and copper, having the formula $2(PbO),CuO,3CrO_3$. The dark-red mineral, which has been termed *melanochroit*, is a *sesquichromate of lead*, $=3PbO,2CrO_3$.

PROTOCHLORIDE OF CHROMIUM ($CrCl$) is formed by passing hydrogen over the sesquichloride at a dull red heat, when a white crystalline mass remains, which at a higher heat fuses, and on cooling presents a fibrous texture.

SESQUICHLORIDE OF CHROMIUM (Cr_2Cl_3) is formed along with the protochloride in the process just described: it is also obtained by evaporating to dryness the hydrochloric solution of the sesquioxide, and heating the residue intensely in a retort, or in a stream of chlorine; it forms a crystalline pink sublimate, which yields a green solution with water.

OXYCHLORIDE OF CHROMIUM; *Chromate of Terchloride of Chromium; Chlorochromic Acid* ($CrCl_3,2CrO_3$).—This compound is obtained by heating a mixture of chromate of potassa, chloride of sodium, and sulphuric acid; sulphate of potassa and sulphate of soda remain in the retort, and the oxychloride of chromium distils over: $3(KO,CrO_3)+3NaCl+6SO_3=3(KO,SO_3)+3(NaO,SO_3)+(CrCl_3,2CrO_3)$. It is a fuming liquid of a deep red color: it decomposes water, forming chromic and hydrochloric acids. When passed through a red hot tube, it is resolved into oxygen, chlorine, and sesquioxide of chromium: $2(CrCl_3,2CrO_3)=3(Cr_2O_3)+O_3+Cl_6$.

TERFLUORIDE OF CHROMIUM (CrF_3) is obtained by distilling 4 parts of chromate of lead, 3 of powdered fluor-spar, and 8 of sulphuric acid, in a platinum retort: the vapor which passes over may be condensed by cold into a red liquid, which is converted by the moisture of the air into chromic and hydrofluoric acids: $CrF_3+3HO,=CrO_3+3HF$.

SESQUISULPHIDE OF CHROMIUM (Cr_2S_3) is formed by passing the vapor of sulphide of carbon through a red-hot porcelain tube containing protoxide of chromium: it is of a dark-gray color, and when heated in the air it burns into oxide. It is a weak *sulphur base*, and forms a few sulphur salts.

SULPHATE OF CHROMIUM.—When a solution of 8 parts of hydrated oxide of chromium in 9 of sulphuric acid is exposed to the air in a covered basin it concretes in a few weeks into a blue-green crystalline mass; when this is dissolved in water, and alcohol added, a blue crystalline compound falls, soluble in about its weight of water at 60°: it consists of $Cr_2O_3,3SO_3,15HO$. With sulphate of potassa it forms a beautiful double salt, which crystallizes in green and purple octahedra, and has been termed *chrome alum*, its formula being $KO,SO_3,+Cr_2O_3,3SO_3,+24HO$. It also forms a similar aluminoid compound with sulphate of ammonia, $=NH_4O,SO_3+Cr_2O_3,3SO_3,+24HO$. This blue sulphate, when heated to 212°, becomes green, losing 10 atoms of water, and though soluble, is no longer crystallizable. If either of these sulphates is heated to about 700°, a red insoluble anhydrous salt remains $=Cr_2O_3,3SO_3$, which, however, by long digestion in water, reverts to the soluble varieties.

TESTS FOR THE COMPOUNDS OF CHROMIUM.—The *sesquisalts* of this metal are of various shades of green, blue, or purple, and their solutions are usually red by transmitted light. 1. With potassa and soda, and their carbonates, they give green precipitates, soluble in an excess of the precipitant, forming green solutions, but again thrown down as anhydrous oxide on boiling the liquid. 2. Ammonia and the hydrosulphate of ammonia throw down a bluish-green hydrated oxide, partially soluble in excess of ammonia, forming a pink solution. Carbonate of ammonia acts in a similar manner.

The *salts of the protoxide* soon absorb oxygen, and are decomposed, or pass into sesquisalts.

The *chromates* are all deeply colored: they are decomposed when boiled with deoxidizing agents (grape-sugar, arsenious acid), and the sesquioxide is formed. A solution of chromate of potassa gives a characteristic yellow precipitate with the soluble salts of lead, orange with those of mercury, and red with those of silver. A compound of chromium fused at a high temperature, with a mixture of carbonate of soda and chlorate of potassa, forms a soluble chromate of the alkali, producing a yellow solution in water, which may be tested in the manner above described. Before the blowpipe, they color borax green in the interior, and yellow or red in the exterior flame.

CHAPTER XXXIV.

VANADIUM—TUNGSTEN—COLUMBIUM—NIOBIUM—ILMENIUM—NORIUM—PELOPIUM—MOLYBDENUM—URANIUM—TELLURIUM—TITANIUM.

VANADIUM (V=68).

THIS metal was discovered in 1830, and named after *Vanadis*, a Scandinavian deity. It occurs in certain lead ores. It may be obtained by decomposing chloride of vanadium by a current of dry ammonia, in a glass tube heated over a spirit-lamp; sal-ammoniac sublimes, and metallic vanadium remains. It may also be obtained by heating vanadic acid with potassium.

Vanadium has a silvery lustre, is brittle, and not acted upon by air or water at common temperatures; at a dull red heat it burns into a black oxide; it is not acted upon by sulphuric or hydrochloric acid, but nitric and nitrohydrochloric acids yield with it dark-blue solutions.

OXIDES OF VANADIUM.—There are three compounds of this metal with oxygen; two oxides, and an acid.—*Protoxide of Vanadium* (VO). When a stream of dry hydrogen gas is passed over heated vanadic acid, water is formed, and a black substance remains, which is infusible, and which, when heated in the air, is converted by slow combustion into the binoxide. It is not salifiable.—*Binoxide of Vanadium; Vanadious Acid* (VO_2). This is the only salifiable oxide: it may be obtained in the state of *hydrate*, by precipitation from its acid solutions by carbonate of soda in very slight excess. It yields blue solutions with the acids, and dissolves in caustic potassa and in ammonia, forming brown liquids.—*Vanadic Acid* (VO_3). When vanadate of ammonia is heated in an open vessel it acquires a red color, and leaves vanadic acid: heated in a close vessel, the hydrogen of the ammonia deoxidizes the acid, and the binoxide is the product. Vanadic acid, when fused, is red, but when in powder, brown: it fuses at a dull red heat, and in the act of cooling it contracts in bulk, and becomes incandescent. It undergoes no change by heat, provided deoxidizing agents are excluded; but when combustible matter is present it passes into oxide: it is tasteless, insoluble in alcohol, and nearly so in water.—*Vanadates.* These compounds are generally yellow, but sometimes are produced colorless, without apparent change of composition, and give a *blue* solution, distinctly opposed to the green of chromium. The soluble vanadates are deoxidized by alcohol, sulphuretted hydrogen, and sulphurous acid. Vanadic acid dissolves and forms colored compounds with the binoxide: they are formed when the binoxide in water is exposed to air; it gradually forms vanadic acid, and the solution becomes blue, green, yellow, and red, according to the extent of acidification.

Vanadium combines with chlorine, bromine, iodine, sulphur, and cyanogen.—*Chloride of Vanadium.* When dry chlorine is passed over a red-heated mixture of protoxide of vanadium and charcoal, in a glass tube, a yellow liquid is obtained, which when acted upon by water yields hydrochloric and vanadic acids: it is therefore a terchloride (VCl_3).—*Sulphide of Vanadium.* By passing sulphuretted hydrogen over the binoxide heated to redness, a *bisulphide* is formed. When sulphuretted hydrogen is passed through vanadic acid in water, a mixture of hydrated binoxide and sulphur is precipitated; but when a solution of vanadic acid in hydrosulphate of ammonia is acidulated by hydrochloric acid, a brown hydrated *tersulphide* subsides.

TUNGSTEN (W=92).

This metal, called also *Wolframium*, was discovered in 1781. It derives its name *tungsten*, from two Swedish words signifying heavy stone. Its native sources are *wolfram*, which is a *tungstate of iron and manganese*, $=MnO,WO_3,+3(FeO,WO_3)$, and *tungstate of lime*, CaO,WO_3. It is obtained by passing hydrogen over ignited tungstic acid mixed with charcoal. It is very difficult of fusion, hard, brittle, and of an iron-gray color. Its specific gravity is 17·6. It is oxidized by the action of heat and air, and by nitric acid. It is also oxidized and gradually dissolved by a solution of potassa, with the evolution of hydrogen, and *tungstate of potassa* is produced.—*Oxide of Tungsten; Binoxide of Tungsten* (WO_2). This oxide may be obtained by mixing finely-powdered wolfram with twice its weight of carbonate of potassa, and fusing it in a platinum crucible. Tungstate of potassa is thus formed, which is dissolved in hot water with half its weight of sal-ammoniac, evaporated to dryness, and heated red-hot in a Hessian crucible. The mass is then well washed in boiling water, and digested in a weak solution of potassa. The residue is oxide of tungsten. Thus prepared, the oxide is black, and when heated to redness it suddenly ignites and burns into tungstic acid. It does not combine with acids. When a current of hydrogen is passed over heated tungstic acid, it is partially deoxidized and converted into a chocolate-colored oxide, which neither combines with acids nor bases, and which is identical in composition with the above. If the action of hydrogen be continued, the oxide itself is reduced.

A compound of this oxide with soda is obtained by adding as much tungstic acid to fused tungstate of soda as it will dissolve, and then passing hydrogen over the compound at a red heat; on washing out the undecomposed tungstate with water, a golden-colored substance remains, in cubes and scales of a metallic lustre, and insoluble in caustic alkalies and in nitric, sulphuric, and nitrohydrochloric acids, but soluble in hydrofluoric acid.

TUNGSTIC ACID (WO_3) is obtained when the oxide is heated red hot, and stirred in an open vessel. When finely-powdered native tungstate of lime is boiled for some hours in nitric acid, tungstic acid is separated, in the form of a yellow powder, which may be freed from adhering nitric acid by dissolving it in ammonia and heating the tungstate of ammonia to redness. Tungstic acid is a yellowish powder, insoluble in water, but soluble in the caustic alkalies, when in its hydrated state; after it has been heated it is difficultly acted upon by solvents, but most of its compounds may be obtained by fusion at a red heat. The tungstate of soda is employed for the purpose of rendering cotton and linen uninflammable. The most delicate lace impregnated with a weak solution of this salt dried and burnt, is converted into carbon without inflaming.

CHLORIDE OF TUNGSTEN (WCl_2).—When tungsten is heated in chlorine, it forms a red crystalline compound, fusible, and volatile, which becomes blue in water.—*Perchloride of Tungsten* (WCl_3). When sulphide of tungsten is heated in chlorine, it forms a *perchloride*, which condenses in red crystals. This chloride is resolved by the moisture of the air into tungstic and hydrochloric acids.

SULPHIDE OF TUNGSTEN.—When sulphuretted hydrogen is passed over tungstic acid heated highly in a porcelain tube, a black powder is obtained, which is a bisulphide $=WS_2$.

CHARACTERS OF THE COMPOUNDS OF TUNGSTEN.—Before the blowpipe, tungstic acid becomes upon charcoal at first brownish-yellow, is then reduced to a brown oxide, and lastly becomes black without melting or smoking. With microcosmic salt, in the internal flame, and in small proportion, it forms a blue-colored glass; if iron is present the color is blood-red.

The tungstates of the alkalies are colorless, and form colorless solutions. When a little hydrochloric acid is added, and a bar of zinc is placed in the solution, the liquid soon acquires a rich blue color from the production of oxide of tungsten. The presence of this metal in any mineral may be thus easily recognized. The substance should be powdered, and fused with four times its weight of carbonate of soda mixed with some nitre. A soluble tungstate is thus produced, which may be tested by the process above described. Mineral acids, excepting the phosphoric, precipitate tungstic acid from solution of tungstates, in an insoluble form.

COLUMBIUM ($Ta=184$).

This metal, called also *Tantalum*, was discovered in 1801, in a mineral from North America (*Columbia*). It was afterwards found in the minerals called *tantalite*, *yttro-tantalite* and *Fergusonite*. Columbium has been obtained by heating potassium with the *potassio-fluoride of columbium*, and washing the reduced mass with water. It remains in the form of a black powder; by pressure it acquires the lustre and color of iron; it burns at a red heat into a whitish oxide. It is insoluble or nearly so, in most acids. Heated to redness, it burns into columbic acid.

OXIDE OF COLUMBIUM; *Tantalous Acid* (TaO_2).—When columbic acid is intensely heated in a charcoal crucible, it is superficially reduced to a metallic state, but the interior portion is a dark-gray oxide, becoming brown when pulverized; it is insoluble in the acids, but may be peroxidized by fusion with potassa.

COLUMBIC ACID; *Tantalic Acid* (TaO_3) is obtained by fusing finely-powdered tantalite with caustic potassa; a soluble columbate of potassa is formed, from which the columbic acid may be precipitated, as a white *hydrate*, by acids. After having been ignited, it is nearly insoluble in acids, but soluble in potassa. The hydrated acid ($TaO_3,3HO$) dissolves in potassa, in nitric, hydrochloric, hydrofluoric, sulphuric, tartaric, citric, and oxalic acids. It is dissolved by a solution of binoxalate of potassa, but scarcely at all by bitartrate of potassa. It is again precipitated from its acid solutions by alkaline carbonates. Ferrocyanide of potassium produces a yellow; infusion of galls an orange; and the hydrosulphates a white precipitate in the oxalic solution. Tantalic acid is precipitated by water from its solution in sulphuric acid, and when this precipitate is dissolved in diluted hydrochloric acid, and a bar of zinc is introduced, the liquid at first acquires a blue color, and afterwards becomes brown. (WILL.)

NIOBIUM. ILMENIUM. NORIUM. PELOPIUM.—Among these rare metals, the two first-mentioned have been announced as associated with columbium in some varieties of tantalite, but their distinctive characters have been as yet very imperfectly ascertained. Niobium is considered by some chemists to be columbium, while the metal pelopium has no independent existence, the pelopic and niobic acids being identical. Von Kobell has announced another metal of this series, to which he has given the name of DIANIUM. He states that it exists in the columbite of Tamméla, in euxenite, and other minerals. Rose and St. Clair Deville, who have examined these minerals, affirm that the supposed dianic acid is hyponiobic acid. Dianium, therefore, is identical with Pelopium and Columbium (*Cosmos*, Janvier, 1862, p. 28.)

Molybdenum ($Mo=48$).

This metal derives its name from the Greek μολύβδαινα, owing to the resemblance of the native bisulphide to plumbago or black lead. It was discovered in 1782. The *bisulphide* is its principal ore; there is also a native *molybdate of lead*. To procure molybdenum, the pulverized native sulphide is roasted in a muffle, so as to burn off the sulphur: a gray powder remains, which is digested in ammonia, and the solution filtered and evaporated to dryness: the dry residue is then dissolved in nitric acid, and again evaporated to dryness, when pure molybdic acid is left. If this be made into a paste with oil and charcoal, and intensely heated, the metal remains. It may also be obtained by passing hydrogen over molybdic acid at a red heat in a porcelain tube.

Molybdenum is a whitish, brittle, and very difficultly-fusible metal; when intensely heated in the air, it produces a white crystalline sublimate of molybdic acid. It forms three compounds with oxygen, two of which are salifiable, and the third an oxide.

Protoxide of Molybdenum (MoO) is obtained by dissolving molybdic acid in hydrochloric acid, and putting a piece of zinc into the solution: the liquid changes to blue, red, and black; excess of ammonia is then added, by which protoxide of molybdenum is thrown down in the form of a black hydrate, whilst the oxide of zinc is retained in solution. In the state of hydrate, this oxide is soluble in the acids, but when anhydrous, it is almost insoluble. It is not dissolved by the caustic and carbonated alkalies, but the recently-precipitated hydrate is soluble in carbonate of ammonia.

Deutoxide of Molybdenum (MoO_2).—This oxide is obtained by heating a mixture of sal-ammoniac and molybdate of soda in a platinum crucible until the fumes cease: the residue is well washed, digested in caustic potassa to separate any molybdic acid, and again washed with boiling water. The oxide remains in the form of a black powder, becoming dark-brown when dry, and purple when exposed to the sun's rays. Although zinc reduces molybdic acid to the state of protoxide, copper only brings it down to deutoxide; if therefore, copper, molybdic acid, and hydrochloric acid are put together, the molybdic acid disappears, and the liquid, which contains the chlorides of copper and molybdenum, acquires a deep-red tint. When an excess of ammonia is added to the liquid, the deutoxide of molybdenum is thrown down, and the oxide of copper is retained in solution; the precipitate is cleansed by washing with solution of ammonia, and when carefully dried *in vacuo* over sulphuric acid, is the hydrated deutoxide. It is brown, slightly soluble in water, and insoluble in saline solutions and in caustic alkalies, but soluble in their carbonates. When heated *in vacuo*, it becomes dark brown, and loses its solubility.

Molybdous Acid.—When metallic molybdenum and molybdic acid are boiled together in water, a blue solution is formed, which has sometimes been termed *molybdous acid*, and regarded as a distinct stage of oxidation, but which appears to be a compound of molybdic acid with the deutoxide, and consequently a molybdate of oxide of molybdenum $=MoO_2,+MoO_3$. When a current of hydrogen is passed over molybdic acid at a dull red heat, it acquires a blue color, and becomes converted into molybdous acid. This compound is soluble in water, and yields a rich blue solution, which becomes colorless on moderate dilution: it is insoluble in a solution of sal-ammoniac; it is immediately converted into molybdic acid by nitric acid and chlorine; and, on the other hand, deoxidizing agents, such as protochloride of tin, or tin filings and hydrochloric acid, convert molybdic acid into this blue compound.

MOLYBDIC ACID (MoO_3).—The production of this acid has already been described. It is a white, difficultly-soluble powder. Heated to redness in an open vessel, it slowly sublimes, and condenses in yellowish scales. It dissolves in hot sulphuric acid, forming a solution which is colorless while hot, but on cooling acquires a blue color, which is heightened by the addition of soda. Its hydrochloric solution is pale yellowish-green, but becomes blue when neutralized by potassa. It dissolves in the alkalies, forming solutions which are colorless, and from which the molybdic acid is at first precipitated, but afterwards dissolved, by the stronger acids. It unites with bases and forms neutral and acid salts.

MOLYBDATE OF AMMONIA (NH_4O,MoO_3).—This salt is obtained by dissolving molybdic acid in excess of ammonia, and leaving it to spontaneous crystallization: it forms square prisms, of a pungent metallic taste. When the ammoniacal solution is boiled down, it affords, on cooling, a crystalline mass of *bimolybdate* of ammonia, which, by spontaneous evaporation, may be obtained in rhombic crystals of a pale bluish-green color, and difficultly soluble in water. A solution of this salt is occasionally employed as a test for phosphoric acid.

PROTOCHLORIDE OF MOLYBDENUM ($MoCl$).—When the vapor of bichloride of molybdenum is passed over molybdenum heated nearly to redness, a deep red compound is obtained, which yields a crystalline sublimate when heated in an open tube: it is insoluble in water, but is decomposed by a solution of potassa, yielding hydrated protoxide of molybdenum. This chloride forms double salts with sal-ammoniac and with chloride of potassium.

BICHLORIDE OF MOLYBDENUM ($MoCl_2$) is formed by heating metallic molybdenum in dry chlorine; the metal burns, and a red vapor fills the retort, which condenses into crystals resembling iodine; they are fusible, volatile, and in the air first fume, and then deliquesce into a black liquid, which changes color in proportion to the water it absorbs, becoming blue-green, green-yellow, dark red, rose-colored, and lastly, yellow. This chloride forms a double *ammonio-chloride of molybdenum* with sal-ammoniac, but does not combine with the chlorides of potassium or sodium.

Chloromolybdic Acid.—When a current of chlorine is passed over gently-heated binoxide of molybdenum, a yellowish crystalline sublimate is formed, and molybdic acid remains in the tube: this compound is less volatile than the bichloride. It readily dissolves in water, and alcohol. It is a compound of molybdic acid with perchloride of molybdenum$=MoCl_3,2MoO_3$.

There are three SULPHIDES OF MOLYBDENUM, two of which correspond with the deutoxide and with molybdic acid, and the third contains 4 equivalents of sulphur; no *protosulphide* corresponding with the protoxide has been formed.—*Bisulphide of molybdenum* (MoS_2) is produced artificially by intensely heating a mixture of molybdic acid and sulphur, out of the contact of air. It forms the *native sulphide.*—*Tersulphide of Molybdenum* (MoS_3) is obtained by saturating a strong solution of a molybdic salt with sulphuretted hydrogen, and then adding hydrochloric acid; a dark-brown precipitate falls, which becomes black on drying, and which, when heated in close vessels, gives off sulphur, and becomes bisulphide. This sulphide combines with the sulphides of the alkaline bases, and produces a class of *sulphur-salts,* which may be called *molybdo-tersulphides,* some of which form beautiful iridescent crystals.—*Persulphide of Molybdenum* (MoS_4) is obtained by saturating bimolybdate of potassa with sulphuretted hydrogen, and boiling the solution for some hours in a retort: when it cools, a black powder, and red scales, are deposited, which must be separated as far as possible: the red deposit is then washed upon a filter with water, till the washings no longer afford a *red* (not a brown) precipitate with hydrochloric acid; the residue upon the filter is then treated by boiling water, and the dark-red solution which filters through, is decomposed by excess of hydrochloric acid: a brown precipitate falls, which, when washed and dried, is the quadrisulphide.

TESTS FOR THE SALTS OF MOLYBDENUM.—1. The *protosalts* give brown precipitates with the alkalies and their carbonates, soluble in excess of carbonate of ammonia, but not of the alkali. 2. Sulphuretted hydrogen gives a brown precipitate, soluble in hydrosulphate of ammonia. 3. The salts of the *deutoxide* give brown precipitates with *ammonia*, and with *ferrocyanide of potassium*. 4. The *molybdates* are characterized by the blue color produced on the addition of a few drops of protochloride of tin, and by the blue color produced by zinc in their solutions, when acidulated with hydrochloric acid. This, after a time, becomes green, and ultimately black. When a mineral containing molybdenum is fused with carbonate of soda and nitre, a soluble molybdate of the alkali is obtained. Molybdic acid is precipitated from its solutions by a mineral acid, but the precipitate is soluble in an excess of the acid. This forms a distinction between the molybdic and tungstic acids. The oxides of molybdenum give to microcosmic salt in the inner flame of the blowpipe, a green color, and to borax a brown-red color.

URANIUM ($U=60$).

Uranium (named from the planet Uranus) was discovered in 1789, in a mineral called *pitchblende*, which is an impure oxide, and from which the metal and its compounds are almost exclusively obtained. It also occurs, in the form of a double phosphate of lime and uranium, in *uranite*, a rare micaceous mineral; and in a similar mineral of a green color, called *chalcolite*, in which the lime is replaced by oxide of copper.

Uranium is obtained by the decomposition of its chloride by sodium, the process being similar to that by which magnesium is obtained: it is white, slightly malleable, and unchanged by air and water at common temperatures; when heated in air it undergoes combustion and is converted into an oxide.

OXIDES OF URANIUM.—Uranium forms four oxides—namely, a protoxide, a sesquioxide, and two intermediate oxides.—*Protoxide of Uranium* (UO) is formed by heating the peroxalate out of contact of air: it is brown, and when in the state of hydrate, dissolves in the acids, forming green salts. When heated to redness, and suddenly cooled, it becomes the *black oxide* (U_4O_5), which is used in porcelain painting for the production of an intense black.—*Green oxide of Uranium* (U_3O_4) is obtained by evaporating an ethereal solution of nitrate of uranium, and exposing the residue to a red heat.—*Per* or *Sesquioxide of Uranium* (U_2O_3). Uranium and its inferior oxides pass into peroxide when acted upon by nitric acid, forming a yellow solution, from which the alkalies throw down compounds of the peroxide with the precipitants. A pure hydrate of the peroxide may, however, be obtained by evaporating the alcoholic solution of the pernitrate until it effervesces in consequence of the escape of nitrous ether; the yellow residue, washed first with cold and then with hot water, leaves the *hydrate*, assuming, when dried at 212°, the form of a yellow powder$=U_2O_3,HO$, but if dried *in vacuo* $=U_2O_3,2HO$. At a high temperature (about 570°) it becomes anhydrous, and afterwards loses oxygen, and leaves a brown mixture of protoxide and green oxide: in its anhydrous state it is red.

The salts of the peroxide of uranium are best formed by the action of nitric acid upon the salts of the lower oxides. They are yellow, and mostly soluble in water, and are reduced to protosalts by sulphuretted hydrogen, and by alcohol and ether under the influence of solar light. Peroxide of uranium unites to bases forming *uranates;* those of the alkalies are obtained by precipitating the uranic salts with them. The uranates of baryta, lime, and magnesia are formed by mixing their salts with those of the uranic oxide, and adding ammonia, but a portion of uranate of ammonia in these cases goes down with them. They are yellow or orange colored compounds.

NITRATE OF URANIUM ($U_2O_3,NO_5,6HO$).—This is the common crystallized nitrate of uranium obtained by evaporating the nitric solution of any of the oxides: it forms yellow prisms, efflorescing in a warm atmosphere into a terhydrate. When heated it fuses in its water of crystallization, becoming orange-colored; and at a red heat leaves green oxide. It is very soluble in water, alcohol, and ether. When its alcoholic solution is gently heated, it effervesces and evolves nitrous ether, depositing hydrated peroxide. Its ethereal solution exposed to the sun's rays deposits green oxide, nitrous ether, and a green solution of protoxide being at the same time formed. When crystallized nitrate of uranium is carefully heated until it becomes orange-colored, a yellow insoluble subnitrate separates: this, at a red heat, passes first into U_3O_4, and then into U_2O_3. This solution sometimes contains lead as an impurity; this will affect the action of tests. The ammonio-nitrate of uranium is of a golden-yellow color, soluble in boiling water with loss of ammonia, but not very soluble in cold water. It is easily dissolved by diluted nitric acid when heated. The solution is rendered pale by an excess of acid.

PROTOCHLORIDE OF URANIUM (UCl) is obtained by passing dry chlorine over a mixture of oxide of uranium with one-fourth its weight of carbon heated to redness in a porcelain tube: red vapors of the chloride are formed, which condense into dark-green crystals: they dissolve rapidly in water, furnishing a dark-green solution, and when exposed to air evolve fumes of hydrochloric acid.

SULPHATES OF URANIUM.—A *sulphate of protoxide of uranium* (UO,SO_3) is formed by adding sulphuric acid to the concentrated aqueous solution of the protochloride: it forms green hydrated crystals, which do not become anhydrous till so highly heated as to begin to lose acid, and which, in a large quantity of water, are resolved into a green acid solution, and a deposit of basic sulphate$=2(UO),SO_3,2HO$, when dried *in vacuo*. This salt forms a crystallizable double sulphate with sulphate of ammonia,$=NH_4O,SO_3,+UO,SO_3$ *Sulphate of green oxide of uranium* is formed by dissolving the green oxide in sulphuric acid, and expelling the excess of acid by heat: it is a pale-green mass$=U_3O_4,2SO_3$. When heated to redness it evolves sulphurous acid, and leaves a pale yellow sulphate of the peroxide: $2(U_3O_4,2SO_3)=3(U_2O_3,SO_3)+SO_2$. *Sulphate of peroxide of uranium* (U_2O_3,SO_3) is obtained by oxidizing the solution of the green oxide in sulphuric acid by nitric acid, or by adding sulphuric acid to a solution of the nitrate, evaporating to dryness, so as to expel the excess of acid, dissolving the residue in water, and concentrating the solution by evaporation to the consistency of syrup: it is slowly and difficultly crystallizable in small yellow prisms$=U_2O_3SO_3,3HO$: dried at 212°, they lose 2 atoms of water, and become anhydrous at 600°. A *phosphate* and *carbonate* of the peroxide of uranium may be obtained by double decomposition. There is also an ammonia-phosphate, which is very insoluble.

TESTS FOR THE SALTS OF URANIUM.—The salts of the peroxide form yellow solutions; an excess of acid renders them pale. 1. *Sulphuretted hydrogen* produces no precipitate. 2. *Hydrosulphate of ammonia* throws down a dark-brown sulphide. 3. *Potassa* or *ammonia* throws down an orange-yellow *uranate*, insoluble in an excess of the reagent, and in hydrochlorate of ammonia. 4. *Alkaline carbonates* (soda and potassa) give a pale yellowish-green precipitate, not soluble in an excess. The precipitate is dissolved by alkaline bicarbonates, and by carbonate of ammonia, but is re-deposited on boiling the liquid. 5. *Ferrocyanide of potassium* gives a deep red-brown precipitate, or color:—ammonia destroys this color, forming a nearly colorless liquid. The color of the precipitate closely resembles that which is produced in a solution of copper; but the ferrocyanide of copper, dissolved by ammonia, produces a blue-liquid. This furnishes a sufficient distinction between the two metals. The carbonate of an alkaline earth (baryta) precipitates the sesquioxide of uranium from its solutions as it does the sesquioxide of iron. With borax the oxide gives, under the blowpipe, a bead which is green in the inner and yellow in the outer flame. With microcosmic salt the color from the outer flame is yellow-green.

Peroxide of uranium is used to give a yellow or a greenish yellow color to glass. The green oxide is employed to produce a black color on porcelain. The *protosalts* of uranium are green, and are rapidly converted into yellow persalts either by exposure to air, or by the action of nitric acid.

TELLURIUM (Te=64).

Tellurium was discovered in 1782. It derives its name from *tellus*, the earth. Its ores are rare, and generally contain it in combination with other metals, especially with gold, silver, lead, copper, and bismuth.

Tellurium is of an iron-gray color, hard, brittle, fusible at a temperature a little above melting lead, and volatile at a full red heat, its vapor condensing in metallic-looking opaque globules in the cold part of the tube. The vapor is yellow, resembling that of selenium. It is partially oxidized and converted into a white uncrystalline oxide, which is deposited around the condensed globules of the metal. It gives a metallic ring resembling somewhat that of arsenic; but it is so much less volatile than arsenic, that it requires for its volatilization, the full heat of Bunsen's jet. Its oxide is not deposited in transparent octahedral crystals. When warmed with sulphuric acid, it imparts to that liquid a splendid amethyst-red color, which is not permanent. If heated on platinum it rapidly melts, combines with, and destroys that metal, forming a very fusible crystalline alloy. When heated on mica, it melts and burns with a bluish flame, having a greenish margin, and it evolves a thick white acid smoke. The color of the flame resembles that of selenium, but has a greenish tint. It traverses a solution of indigo, giving a pale blue light. Although closely resembling selenium, yet it differs in readily forming a fusible alloy with platinum, and in evolving no reddish-colored fumes when heated in air. Its sp. gr. is 6·2 to 6·8. It is crystallizable, and, for a metal, it appears to be a bad conductor of heat and electricity: indeed, it may be said, in some respects, to form a connecting link between sulphur or selenium and the metals. By some chemists it is placed among the metalloids, between selenium and phosphorus.

BINOXIDE OF TELLURIUM; *Tellurous Acid* (TeO_2).—Exposed to heat and air, tellurium fuses and burns, exhaling a peculiar sour odor, and forming a white oxide. This oxide is thrown down as a white hydrate when a recently made solution of tellurium in nitric acid is poured into water. In its anhydrous state it is difficultly soluble, but when hydrated, it readily dissolves in most of the acids, forming colorless solutions of a nauseous metallic taste: they afford metallic tellurium in a black powder when acted on by phosphorous acid, or sulphurous acid, as well as by zinc, iron, tin, lead, copper, and some other metals. Most of the solutions of this oxide in the mineral acids are decomposed by copious dilution with water, provided there is no great excess of acid; with the alkalies and their carbonates they give precipitates of hydrated oxide soluble in excess of the precipitant, especially when aided by heat: they are precipitated white by phosphate of soda; dark-brown by sulphuretted hydrogen and alkaline hydrosulphates; and yellow by tincture of galls; they are not affected by ferrocyanide of potassium, nor by oxalic acid. The basic combinations of tellurous acid, or *tellurites*, are obtained: 1. by dissolving the hydrated acid in the alkalies; 2. by double decomposition; or 3 by fusion. The alkaline tellurites are soluble in water: those of baryta, lime, and strontia with difficulty; most of the other compounds are insoluble in water; but they are nearly all soluble in hydrochloric acid.

PEROXIDE OF TELLURIUM; *Telluric Acid* (TeO_3) may be obtained by passing chlorine through the solution of tellurous acid in excess of potassa till it is fully saturated, and the first precipitate is redissolved. The filtered liquor is then neutralized by ammonia, and chloride of barium added, which occasions a precipitate of tellurate of baryta; this, digested with a fourth of its weight of sulphuric acid (diluted with water), yields a solution, which, when filtered and carefully evaporated, affords crystallized hydrated telluric acid$=TeO_3,3HO$, from which adhering sulphuric acid may be removed by alcohol. This hydrate loses its water by heat, and the *anhydrous acid*, of a lemon-yellow color, remains. This acid is readily procured as a tellurate by fusing tellurium with nitre, and when this is calcined with charcoal and carbonate of potassa, telluride of potassium is obtained. Anhydrous telluric acid is insoluble in water; but the crystallized acid dissolves in boiling water. When boiled with hydrochloric acid it forms tellurous acid, and like selenic acid, sets free chlorine (p. 216). Dried at 320°, the crystals lose 2 atoms of water, and become anhydrous at a temperature a little below redness. The *tellurates* of the alkalies are moderately soluble in water; those of the alkaline earths are sparingly soluble; and many of the other tellurates are insoluble. When tellurium is heated in chlorine it burns, forming a dark liquid, which by an excess of chlorine becomes yellow, and concretes on cooling into a white deliquescent crystalline *bichloride*, $=TeCl_2$. If this is heated with pulverized tellurium, a dark purple protochloride is formed, $=TeCl$, more volatile than the bichloride, and giving a vapor resembling that of iodine.

TELLURETTED HYDROGEN (TeH).—When an alloy of tellurium and tin, or zinc is acted on by hydrochloric acid, *telluretted hydrogen gas* is evolved; it reddens litmus, dissolves in water, and possesses the general properties of sulphuretted hydrogen, which it also resembles in odor. Its sp. gr. is 4·48.

There appear to be two sulphides, which act as *sulphur acids;* they are obtained by the decomposition of tellurous and telluric acids by sulphuretted hydrogen.

TESTS FOR THE COMPOUNDS OF TELLURIUM.—The solutions of tellurium in mineral acids are decomposed by the immersion of zinc, tin, lead, copper, or cadmium, and the metal is precipitated in the form of a black powder. Tellurous acid and its salts are decomposed when an excess of hydrochloric acid is present, by boiling them with sulphurous acid, or alkaline sulphites, by protosulphate of iron, and protochloride of tin, which occasion a brown or black flocculent precipitate of tellurium. Sulphuretted hydrogen throws down a black bisulphide of tellurium, which is soluble in hydrosulphate of ammonia. The telluride of potassium procured by the method above described blackens silver and evolves telluretted hydrogen when treated with acids.

TITANIUM ($Ti=24$).

Titanium was first detected in a mineral, found in the form of a black sand, in the vale of Menachan, in Cornwall, consisting of the oxides of titanium and iron. In the state of titanic acid it exits in the minerals called Rutilite, Anatase, and Oysanite. Titanite is a silicate of titanium and lime: it occurs in quartz and granite, and it sometimes traverses rock-crystal in brown hair-like filaments. Titanium, as titanic acid, is frequently found in clays and sands, associated with silica and oxide of iron. It is also found in the slags of some iron furnaces; they contain small copper-colored cubic crystals, of a sp. gr. of 5·3; insoluble in the acids, but oxidized by fusion with nitre. They appear to be a combination of nitride with cyanide of titanium, and contain about 18 per cent. of nitrogen and 4 of carbon. Another nitride is obtained in the form of copper-colored scales by passing ammonia over the ammonio-chloride of titanium heated to redness. These nitrides were formerly regarded as pure titanium. To obtain titanium, the potassio-fluoride is decomposed by potassium, when the metal remains in the form of gray particles, which burn brilliantly if heated in oxygen.

PROTOXIDE OF TITANIUM (TiO).—When titanic acid is subjected to a white heat in a charcoal crucible, it is superficially reduced; but the interior is in the state of a black powder, which is the protoxide. When a plate of zinc is immersed in a solution of chloride of titanium, a purple powder is obtained, which is a hydrated sesquioxide (Ti_2O_3,HO).

PEROXIDE OF TITANIUM; *Titanic Acid* (TiO_2) may be obtained from *rutilite*, by fusing it, in fine powder, in a platinum crucible, with thrice its weight of carbonate of potassa: a gray mass is obtained, which, after having been washed with water, is dissolved in hydrochloric acid, and on diluting with water, and boiling the solution, the greater part of the titanic acid is precipitated; it may be collected and washed with very dilute hydrochloric acid. The acid is more perfectly precipitated by adding sulphite of soda and boiling the liquid. Titanic acid is white, infusible, and very difficult of reduction: its sp. gr. is 3·93. When calcined it becomes yellow, and is then dissolved only by concentrated hydrofluoric or sulphuric acid. When recently precipitated, it dissolves in some of the acids, but becomes nearly insoluble after it has been ignited; and like oxide of tin, it is susceptible of two isomeric modifications. When its solution in hydrochloric acid is heated to the boiling-point, a part of the titanic acid is thrown down; but by slow evaporation a soluble chloride remains. It is precipitated by the pure and carbonated alkalies, including ammonia and its carbonate, in a gelatinous form: infusion of galls and ferrocyanide of potassium throw it down of a characteristic red-brown color, and the precipitate is soluble in an excess of the solution of the ferrocyanide. Sulphuretted hydrogen produces no precipitate in the hydrochloric solution. Titanic acid which has been rendered yellow by ignition is sometimes used in enamel and porcelain painting, to give a yellow color. Titanic acid is thrown down from its solution in hydrochloric acid, by alkalies and the alkaline carbonates, and the precipitates are insoluble in an excess of the reagents. The precipitates are, however, dissolved by strong acids.

BICHLORIDE OF TITANIUM ($TiCl_2$) is obtained by passing dry chlorine over metallic titanium, or over a mixture of titanic acid and charcoal heated to redness. It is a dense, transparent, and colorless fluid, fuming when exposed to air. It boils at 277°; the density of its vapor is 6·836. With a small quantity of water it forms a crystalline hydrate, which, by the further addition of water, deposits titanic acid.

BIFLUORIDE OF TITANIUM (TiF_2).—Titanic acid readily dissolves in hydrochloric acid. When this solution is saturated with potassa and evaporated, a *titanofluoride of potassium* is the result.

BISULPHIDE OF TITANIUM (TiS_2) is obtained by passing the vapor of sulphide of carbon over ignited titanic acid. It has a dark-green or bronze color, and a metallic lustre.

None of the other metals appear so to combine with titanium as to form definite alloys; but when it is blended with some of them by fusion, it is susceptible of oxidation, and is then soluble in acids which do not otherwise act upon it.

Tests for the Salts of Titanium.—Titanium is not thrown down in the metallic state by any other metal. The orange-red precipitate, which its solutions afford with infusion of galls and with ferrocyanide of potassium, is very characteristic. When titanic acid is fused on charcoal with carbonate of soda and cyanide of potassium, it does not, like tin, yield any metallic globule. In ordinary analyses of silicates, titanic acid is liable to be precipitated with, and estimated as, oxide of iron, or to be weighed as silica. The best method of separation is probably the following: Fuse the mineral containing titanic acid with four times its weight of carbonate of soda, and remove all that can be dissolved by cold water. The residue will be a titanate of the alkali and oxide of iron. Digest this in concentrated hydrochloric acid, by which the iron and titanic acid are dissolved; then boil the solution, diluted with water, with sulphite of soda—titanic acid alone is precipitated. This may be redissolved in hydrochloric acid, and a bar of zinc introduced into the liquid. If titanic acid is present, it is reduced to the state of sesquioxide, which is dissolved, and gives a blue color to the liquid. By a continuance of the action it is still further reduced, and the oxide of titanium is precipitated as a violet-colored powder.

CHAPTER XXXV.

Antimony ($Sb=129$).

Antimony, or *stibium*, was first made known towards the end of the fifteenth century. It is found *native*, but its principal ore is the *sulphide*, the *stibium* of the ancients. Antimony is obtained from the sulphide by mixing 8 parts of it in fine powder, with 6 of tartar, and 3 of nitre, and projecting it by spoonfuls into a red-hot crucible. The sulphur is oxidized by the nitre, and the metal collects at the bottom. If the metal is required perfectly pure, the pure oxide must be reduced by charcoal.

Antimony is of a bluish-white color, brittle, and crystalline, so that when broken it exhibits splendid facets, and the surface of the ingot as it has cooled in the crucible is often stellated. It fuses at about 840°, or at a dull red heat: it is slowly volatile at a white-heat and in the absence of air, but in a stream of hydrogen it may be distilled. Its sp. gr. is 6·7. Placed upon ignited charcoal, under a current of oxygen, antimony burns with great brilliancy, throwing off a dense yellow smoke; and if a globule of the intensely-heated metal be thrown upon the floor, or upon a black board, it subdivides into numerous smaller globules, which burn as they roll along, and leave a series of white or yellowish lines of oxide. The metal is not dissolved by hydrochloric acid, but readily by nitrohydrochloric acid. It is oxidized when heated with nitric acid, leaving a white residue, insoluble in nitric but soluble in tartaric acid.

Antimony and Oxygen.—There are two well-defined compounds of antimony with oxygen, a *teroxide*, SbO_3, and *antimonic acid*, SbO_5. A third oxide is sometimes described under the name of *antimonious acid*, SbO_4, but it should rather be regarded as an *antimoniate of oxide of antimony* (SbO_3, SbO_5).

Teroxide of Antimony (SbO_3) is formed by heating the metal in air to its point of combustion, when the vapor burns with a bluish flame; and by placing the crucible in an inclined position, acicular crystals of the oxide are deposited in its upper part, forming the *flores antimonii* and *nix stibii* of the older chemists. It may also be formed by adding 50 parts of finely-powdered metallic antimony to 200 of sulphuric acid, boiling the mixture to dryness, and washing the dry mass, first in water and then in a weak solution of carbonate of soda: a white powder remains, which, when thoroughly washed with hot water, is the teroxide. Teroxide, or, as it is sometimes called, protoxide of antimony is white, fusible, and volatile at a high red heat, undergoing no change in close vessels, but condensing in acicular and octahedral crystals; after fusion it concretes into a silky crystalline mass: if air be present, it burns like tinder, and passes into a higher state of oxidation. It is soluble in hydrochloric and tartaric acids, and it forms emetic tartar when boiled in a solution of bitartrate of potassa. It occurs *native*, forming the *white ore of antimony.*

Teroxide of antimony forms compounds with many bases, and in various atomic proportions: most of them are decomposed by water, which becomes milky from the deposition of a subsalt. These compounds have been termed *antimonites.* The teroxide is precipitated from its solution in hydrochloric acid by potassa as a white hydrate, which is dissolved by an excess of the alkali. If to this alkaline liquid, nitrate of silver is added, a black antimonide of silver (Ag_3,Sb), quite insoluble in ammonia, is thrown down. When chloride of gold is added, there is a dark purple precipitate of reduced gold. The teroxide, when heated in a reduction tube, melts into a yellow liquid, and is only partially volatilized in octahedra by the heat of a spirit-lamp. The analogous compound of arsenic is entirely volatilized in brilliant octahedral crystals without melting.

ANTIMONIOUS ACID, or *Antimonite of Antimony* (SbO_3SbO_5, or $2SbO_4$), is the result of the above-mentioned combustion of the protoxide: it is also obtained by exposing antimonic acid to a red heat. It is white in its ordinary state; and it is fixed and infusible in the fire. It is thus distinguished from the teroxide. It also differs from this oxide in being less soluble in hydrochloric acid. Antimonious acid differs from antimonic acid by its remaining white when heated in a close vessel or tube, and by its not evolving oxygen under these circumstances.

ANTIMONIC ACID; *Peroxide of Antimony* (SbO_5) is procured by acting for a considerable time upon the finely powdered metal by an excess of hot nitric acid, and exposing the product to a heat not exceeding 500°. It is of a pale yellow color, tasteless, and insoluble in water. It neither fuses nor volatilizes at a bright red heat, but loses oxygen, and becomes antimonious acid. It does not decompose the alkaline carbonates in the humid way, but at a red heat it expels their carbonic acid, and combines with the base. It dissolves, but not readily, in a boiling solution of caustic potassa, from which it is thrown down by an acid in the form of a *white hydrate*, $SbO_5,4HO$. In this state it reddens litmus and dissolves in hydrochloric acid, and in the alkalies. In the anhydrous state it is only partially dissolved by hydrochloric acid. An acid solution of this oxide is precipitated by a current of sulphuretted hydrogen, as an orange-yellow pentasulphide of antimony. No precipitate is produced by this gas in an alkaline solution of hydrated antimonic acid; and if free from teroxide it does not reduce the salts of silver and gold.

Antimoniates.—Antimonic acid in combination with bases forms neutral and acid salts. *Antimoniate of potassa* is formed by heating 1 part of powdered metallic antimony with 4 of nitre, in an earthen crucible, and washing the pulverized product with water. Its formula is $2(KO),SbO_5$. When this salt is boiled for some hours in water, it is partly converted into a soluble hydrated *antimoniate*, and an insoluble *biantimoniate* $=KO,2SbO_5$. A soluble biantimoniate, supposed to contain a modified acid (*metantimonic* *acid*), is obtained by deflagrating antimony with nitre, washing, and boiling the product so as to convert it into the state of soluble antimoniate, and evaporating this solution in a silver basin to the consistence of syrup: caustic potassa is then added, and the evaporation is continued till a drop of the solution, placed upon a cold piece of glass, crystallizes; it is then set aside to cool, and the crystallized salt dried upon a porous tile. This *bimetantimoniate of potassa* has the formula $KO,HO,SbO_5=6Aq$. It has been used as a test for soda, with which it furnishes an insoluble precipitate; but its indications are very uncertain, and the test itself, when kept for a few days in solution, passes into the *neutral* antimoniate, which does not precipitate soda. The insoluble *bimetantimoniate of soda* is represented as $NaO,HO, SbO_5,6Aq$. Considerable uncertainty hangs over the nature of these modifications of the antimonic acid and the antimoniates, the difference in their properties probably depending upon peculiarities of molecular constitution, which confer distinct characters upon compounds similarly constituted.

Antimony and Hydrogen.—*Antimonuretted hydrogen gas* (SbH_3) is formed by the action of dilute sulphuric or hydrochloric acid on an alloy of zinc and antimony; or by adding an acid solution of oxide of antimony to zinc. The gas is colorless, nearly inodorous (if free from arsenic), and is decomposed when passed through a tube heated to dull redness, depositing a brilliant coat of metallic antimony. It burns in the air with a pale greenish-white flame, producing a white smoke consisting of oxide of antimony, and if the flame be in contact with glass or porcelain, metallic spots are formed somewhat resembling those produced by a similar combustion of arseniuretted hydrogen. It instantly decomposes the salts of silver, precipitating a black antimonide of silver ($SbH_3+3AgO=Ag_3Sb+3HO$), but it produces no change of color in paper impregnated with a solution of a salt of lead. In contact with water the gas rapidly undergoes decomposition, and deposits metallic antimony in the form of a black powder. (*See* Arseniuretted Hydrogen, p. 439.)

Antimony and Chlorine; Terchloride of Antimony ($SbCl_3$).—Antimony takes fire when thrown in fine powder into gaseous chlorine, and a mixed chloride is formed. The terchloride is usually obtained by the distillation of 3 parts of powdered metallic antimony with 8 of corrosive sublimate ($Sb+3HgCl=SbCl_3,+3Hg$), or by dissolving oxide of antimony in hydrochloric acid, and evaporating to dryness out of the contact of air. It is a soft solid at common temperatures, but becomes liquid by a gentle heat, and crystallizes as it cools. It is the *butter of antimony* of old writers. It deliquesces by exposure to air. When water is added to it a mutual decomposition ensues, and hydrated oxychloride of antimony and hydrochloric acid result ($6SbCl_3+15HO=15HCl+SbCl_3,5SbO_3$). This white basic compound resembles that of bismuth in its mode of production and insolubility. It is distinguished from the bismuthic precipitate by its being entirely dissolved by tartaric acid.

Perchloride of Antimony; Pentachloride of Antimony ($SbCl_5$), is formed by passing dry chlorine over heated antimony, or by exposing the terchloride to a stream of dry chlorine. It is a volatile transparent liquid, which emits fumes when exposed to air. When heated it becomes terchloride by the evolution of chlorine. By exposure to air it becomes a crystalline *hydrated perchloride*, which is deliquescent and soluble without decomposition in hydrochloric acid.—*Oxychloride.* When chloride of antimony is mixed with a large quantity of water, a precipitate falls, ($5(SbO_3)SbCl_3$) which was formerly used as an emetic, under the name of *Algarotti's powder*, or *Mercurius vitæ.* The same compound is formed on diluting a solution of antimony in nitro-hydrochloric acid. When first thrown down it is white and curdy, but afterwards assumes a yellowish-gray color and becomes pulverulent or crystalline. By continued washing with hot water, and by the action of alkaline carbonates, it leaves the oxide of the metal. Antimony combines with bromine and iodine, forming compounds analogous to the chlorides.

Tersulphide of Antimony (SbS_3).—This compound may be formed by fusing the metal with sulphur. Its color is dark-gray and metallic; its specific gravity 4·66 : it closely resembles the *native sulphide.* When exposed under a muffle to a dull red heat, it gradually loses sulphur, and absorbs oxygen, being converted into a gray powder, which consists of a mixture of oxide and sulphide. If the heat be increased, this fuses into a transparent substance formerly called *Glass of antimony.* Compounds of the oxide with larger quantities of the sulphide, have been termed *Saffron of antimony* or *Crocus metallorum,* and *Liver of antimony.*

Hydrated tersulphide of antimony is thrown down in the form of a reddish-brown or orange-colored precipitate, when sulphuretted hydrogen is passed through antimonial solutions, and when carefully dried it retains its color, but if it be heated it darkens, and becoming anhydrous, assumes a metallic appearance. It dissolves in solutions of the sulphides of the alkaline metals, which take it up largely when heated, and deposit a portion of it on cooling; it is thrown down from these solutions by acids. Hydrochloric acid dissolves it with evolution of sulphuretted hydrogen, producing a colorless terchloride.

A hot solution of sulphide of antimony in caustic or carbonate of potassa, deposits a brown powder on cooling, formerly called *Kermes mineral;* it is sulphide mixed with oxide of antimony, retaining a little of the alkali. If hydrochloric acid be added to the filtrate, after the deposition of the Kermes, sulphuretted hydrogen escapes, and the remaining sulphide of antimony is thrown down, with some excess of sulphur, and a variable proportion of oxide of antimony. This compound is the *golden sulphide of antimony* of pharmacy, but, like Kermes, it is of uncertain composition. The *red ore of antimony* is a native oxysulphide, $=2SbS_3+SbO_3$.

Native sulphide is by far the commonest ore of antimony. It occurs in prismatic and acicular crystals. It was known to the ancients, and used by the Asiatic and Greek ladies as a pigment for the eyelashes: it was called *stimmi* (στίμμι) and *stibium* (στιβί). It is known in commerce as *crude antimony,* and is usually met with in conical masses or loaves, presenting a dark-gray crystalline fracture; its powder is nearly black, and its melting-point somewhat above that of the pure metal: it is seldom pure, frequently containing the sulphides of lead, iron, copper, and arsenic, the arsenical impurity forming sometimes 1·33 per cent.

Pentasulphide of Antimony; Sulphantimonic Acid (SbS_5) is formed by passing sulphuretted hydrogen through pentachloride of antimony dissolved in aqueous tartartic acid. It is an orange-colored powder, which, when heated out of contact of air, loses 2 atoms of sulphur; it dissolves in warm aqueous ammonia, and in potassa and soda, and combines with the basic sulphides, forming compounds which have been called *sulphantimoniates.* One of the most remarkable of these is the tribasic *sulphantimoniate of sodium* ($3NaS,SbS_5+18Aq$): it is obtained by mixing 18 parts of finely-powdered tersulphide of antimony, 12 of dry carbonate of soda, 13 of quicklime, and 3·5 of sulphur, triturating this mixture with a little water, and then putting it into a well-closed bottle filled with water, and allowing it to digest, with frequent agitation, for twenty-four hours; the clear liquor is then filtered and evaporated *in vacuo* over sulphuric acid; it crystallizes in transparent tetrahedra.

Alloys of Antimony.—With *potassium* and *sodium* antimony forms white brittle compounds. The alloy of potassium and antimony may be procured by heating to redness in a covered crucible a mixture of equal parts of finely-powdered antimony and tartar for about three hours. By substituting tartrate of soda for common tartar, the alloy of sodium and antimony may be obtained: and a mixture of soda-tartrate of potassa and powdered antimony yields the triple alloy of antimony, potassium, and sodium. When these alloys are reduced to powder, and exposed to air, they heat, and take fire like pyrophori (p. 40), and if blended with excess of carbon they burst into sudden ignition on exposure, especially on the addition of a few drops of water. Antimony and *iron* combine by fusion, and form a white alloy: 2 parts of sulphide of antimony fused with 1 of iron, yield a slag of sulphide of iron, and an alloy formerly called *Martial regulus.* This alloy may be recognized by its magnetic properties. *Zinc* and antimony form a hard brittle alloy. Antimony and *tin* may be fused together in various proportions: an alloy of 1 atom of each is brittle and pulverizable: 1 part of antimony and 10 parts of tin form a ductile compound, which a little lead renders brittle. A fine pewter is said to consist of 12 parts of tin and 1 of antimony, with a small addition of copper. An alloy of 1 of antimony and 3 of *copper* is lamellar and brittle, but takes a good polish. When there is excess of antimony the alloy is white. *Type metal* is a compound of 4 parts of *lead* and 1 of antimony; its hardness is such as to resist the pressure to which in the printing-press the type is necessarily subjected: it is readily fusible, and takes a very sharp impression from the matrix or mould in which the letter or stereotype plate is cast. A good *white metal,* used for spoons and tea-pots, called *Britannia metal,* is composed of 100 tin, 8 antimony, 2 bismuth, and 2 copper. Antimony readily combines and forms a fusible alloy with platinum.

TESTS FOR THE COMPOUNDS OF ANTIMONY.—1. The compounds of antimony, when dissolved in water, or in an acid, are decomposed by the immersion of a plate of *zinc;* the metal is thrown down in the form of a black powder, and when hydrogen is evolved a portion of antimony escapes with this gas. 2. *Sulphuretted hydrogen* produces a distinctive brownish-red or dark orange precipitate in salts of antimony with excess of acid, but if they are neutral, their color is only changed, and the precipitate does not ensue until an acid (tartaric) is added. 3. The *alkaline hydrosulphates* produce a similar precipitate, which is soluble in an excess of the precipitant, especially when aided by heat. The precipitate is insoluble in ammonia, but is dissolved by potassa. 4. Many of the combinations of antimony are decomposed when largely diluted with *water,* and a basic salt is thrown down: this decomposition is prevented by the presence of an excess of tartaric acid. (*Distinction from Bismuth,* see p. 407.) 5. *Ammonia* and the *carbonate* of ammonia throw down teroxide of antimony completely from its solutions as a white precipitate, insoluble in an excess of either precipitant. 6. *Potassa* throws down a white hydrated oxide, soluble in an excess of the alkaline liquid. Nitrate of silver added to this alkaline solution of the oxide, produces a black precipitate, insoluble in ammonia; and chloride of gold produces in it a purple-black precipitate. 7. *Ferrocyanide of potassium* gives a white precipitate, having frequently a bluish tint from the presence of iron.

These results are not obtained in a solution of tartar emetic, or the double tartrate of antimony and potassa. 1. Sulphuric, nitric, and hydrochloric acids produce white precipitates (basic salts) in a solution of the double tartrate. These precipitates are readily dissolved by an excess of tartaric or hydrochloric acid. 2. The alkalies and alkaline carbonates do not precipitate the solution except at a boiling temperature. 3. It is not precipitated by ferrocyanide of potassium. 5. It is not readily precipitated by sulphuretted hydrogen until an acid is added, and for this purpose the tartaric acid is preferable: an orange-red precipitate, characteristic of oxide of antimony, is thrown down. This precipitate is distinguished from many other sulphides by its solubility in sulphide of ammonium, and in solution of potassa—as well as by its insolubility in ammonia. If collected and dried, it may be dissolved by heat in a small quantity of strong hydrochloric acid; and when all the sulphuretted hydrogen has escaped, it will be found that, on adding this solution to water, a white oxychloride of antimony is precipitated, possessing the characters elsewhere described (p. 428). A portion of the sulphide, dissolved in hydrochloric acid may be introduced with zinc and sulphuric acid into a Marsh's apparatus. The gas which escapes at the jet produces a deep black deposit on paper impregnated with a solution of nitrate of silver; but unless sulphur is present it produces no change on paper impregnated with a salt of lead. When ignited the gas burns with a pale yellowish-white flame, producing white fumes of teroxide of antimony (p. 428). Porcelain, or glass, depressed on the flame receives a black deposit of finely-reduced metallic antimony, with grayish-colored layers of oxide at the circumference. There is no metallic lustre, such as is produced by arsenic under similar circumstances; but on examining the reverse side of the glass, a metallic lustre will be perceptible. If a current of the gas is heated to redness in a tube, a ring of metallic antimony will be deposited close to the heated spot. This is much more fixed than the deposit of arsenic, and cannot, like it, be resolved into a white sublimate of transparent octahedral crystals. If the gas is made to pass through a small quantity of fuming nitric acid containing nitrous acid, it is decomposed, the antimony is peroxidized, and may be obtained as a white, insoluble residue, on evaporation. A solution of nitrate of silver produces no change in this deposit; but if one or two drops of ammonia are added, there is a black deposit of antimonide of silver (Ag_3Sb). Compounds of antimony heated with carbonate of soda or cyanide of potassium in the reducing flame of the blowpipe, yield globules of metal, surrounded by a white incrustation on the charcoal.

ANALYSIS IN CASES OF POISONING.—The suspected liquid, if clear, may be acidulated with tartaric acid, and a current of sulphuretted hydrogen passed into it. The precipitated sulphide may be easily identified by the characters above described. The contents of the stomach, or the coats of the organ, may be boiled in hydrochloric or tartaric acid, and the filtered liquid subsequently decomposed by the gas.

The following method of detecting antimony, when dissolved in any organic liquid, is based upon the principle by which copper and other metals may be detected under similar circumstances (page 395). Acidulate a portion of the suspected liquid with hydrochloric acid, and place it in a shallow platinum capsule. Touch the platinum, through the acid liquid, with a piece of pure zinc foil. Wherever the metals come in contact, metallic antimony in the state of a black powder, is deposited upon the surface of the platinum. The liquid should be poured off, and the capsule thoroughly washed with distilled water. This may be effected without disturbing the deposit. A small quantity of hydrosulphate of ammonia poured on the black deposit speedily dissolves it (if antimony) by the aid of heat, and on evaporation, an orange-red sulphide of antimony remains. This may be dissolved by a few drops of strong hydrochloric acid, and on adding the acid liquid to water, hydrated oxychloride of antimony is precipitated. By this process antimony in small quantity may be detected in any liquid containing organic matter. Some portion of the metal escapes with the hydrogen. The quantity of antimony may, however, be so small, or the metal may be so diffused through the animal substance (in the tissues), that this process will yield no evidence of the presence of antimony. The parts should then be finely cut up, and boiled in a mixture of one part of hydrochloric acid, and five parts of water. After some time, the liquid may be tested by introducing into it a slip of polished copper foil free from antimony. If antimony is present in small quantity, the copper will acquire a violet-colored deposit on its surface : if in large quantity, the deposit will be gray with a metallic lustre, or sometimes in the state of a black powder. Having obtained a deposit on several slips of copper foil, these may be washed, dried, and heated in a strong solution of potassa (free from lead), with occasional exposure to air, until the metallic deposit is removed. The antimony is thereby oxidized and dissolved by the potassa. A current of sulphuretted hydrogen gas may then be passed into the alkaline liquid. This will throw down any lead that may be accidentally present. Filter the alkaline liquid and acidulate with hydrochloric acid : the orange sulphide of antimony is deposited, and may be collected and examined by the methods above described.

Zinc separates metallic antimony, in the form of a black powder, from the acid solutions of its oxides. This is one of the difficulties attendant on the use of Marsh's process for the detection of antimony. The greater part of the metal is deposited in the tube as a black flaky precipitate, and in the course of a short time, barely a trace of antimony will be found issuing with the hydrogen from the jet.

The following method admits of the separation of antimony from organic substances when the metal is in mere traces. Coil a portion of pure zinc foil round a portion of clean platinum foil, and introduce the two metals into the hydrochloric-acid decoction of the tissues, sufficiently diluted to prevent too violent an action on the zinc. Warm the organic liquid, and suspend the coils in it. Sooner or later, according to the quantity of antimony present, the platinum will be coated with an adhering black powder of metallic antimony. Wash the platinum foil, and digest in strong nitric acid. So soon as the antimony is dissolved from its surface, the platinum may be removed. Add a few drops of hydrochloric acid, and evaporate the acid liquid to dryness. The residue, redissolved in hydrochloric acid, and the solution diluted and treated with a current of sulphuretted hydrogen, will yield an orange-red sulphide of antimony. The black deposit is readily dissolved by sulphide of ammonium, yielding an orange-red sulphide of antimony, and it is also soluble in nitrohydrochloric acid, but not in hydrochloric acid alone. When kept for a few days in contact with water and air, the black metallic deposit is converted into white oxide of antimony.

CHAPTER XXXVI.

ARSENIC (As=75).

THE distinct metallic characters of arsenic were first noticed in 1773, but some of its combinations (the sulphides) were known before the Christian era. Its name is derived from the Greek ἀρσενικὸν (*orpiment*). Its chemical relations are such as to place it rather among the simple acidifiable substances than among the metals : it, however, has the lustre and opacity of a metal, and conducts electricity. It occurs *native*, and in form of *native oxide ;* and there are many native *arsenates*: it also occurs as a *sulphide*, and is frequently found in combination with other sulphides, especially with sulphide of iron, constituting *arsenical pyrites*=FeS_2,$FeAs$. It is owing to its presence in pyrites that arsenic is found in coal and lignite. It has been detected in the coal of Northumberland and Nottingham. The coal of Sarrebrück was found to contain 0·003 per cent. of arsenic, and in a variety of French coal from Villé, as much as 0·0415 per cent. of arsenic was detected (Percy's *Metallurgy*, p. 106). During the roasting of the arseniferous sulphides of copper, iron, cobalt, and nickel, large quantities of oxide of arsenic are formed, and from such sources, commercial demands are supplied. Traces of arsenic are found in many minerals, and consequently in some of their products, as in sulphur and sulphuric acid, in zinc, in sulphide of antimony, and occasionally in phosphorus. It was at one time supposed that arsenic entered into the composition of the flesh and bones of animals as a normal constituent, but it has been clearly proved that it is never found in the tissues, either of animals or vegetables, except when it has been introduced into them by accident or design. It is thus remarkably contrasted with phosphorus, which is an essential constituent of organic matter. On the other hand, the chemical analogies between these elements are in some respects striking. In vapor, they have a similar odor: they form solid acids with oxygen, similar in composition (AsO_3, PO_3 and AsO_5, PO_5), and similar gaseous compounds with hydrogen (AsH_3, PH_3). Their volume equivalents are the same, the atomic weight of each element being represented by half a volume of vapor.

Arsenic may be obtained from the purified *white arsenic* of commerce, by mixing it with its weight of *black flux*, and introducing the mixture into a flask or small retort, gradually raised to a red heat: a brilliant metallic sublimate of arsenic collects in the upper part of the flask or retort. The volatility of white arsenic prevents its easy reduction by charcoal alone; but the potassa in the flux enables it to acquire a temperature sufficient for its reduction. Dried ferrocyanide of potassium is an excellent reducing agent in all cases where it is desired to obtain the metal from arsenious acid. Arsenic may also be obtained by heating the ore called *native arsenic* in coarse powder in a retort; the metal sublimes, leaving the impurities behind.

Arsenic is of a steel-gray color, crystalline texture, and very brittle. Its sp. gr. is 5·75. It volatilizes when heated, and in close vessels may be sublimed at a temperature lower than its fusing point; this is generally stated to be about 400°, but according to Fischer it does not rise in vapor below a dull red heat. The density of arsenic-vapor is about 10·39. Metallic arsenic tarnishes on exposure to air, falling to a grayish-black powder (suboxide?). It gives off no vapor. It does not decompose water, and is not dissolved by that liquid, although it is slowly oxidized by air and water. It has no taste and no odor at ordinary temperatures; but in the state of metallic vapor, as it is liberated by heating its oxide with carbon, it has an odor resembling that of garlic. When boiled in water with a strong solution of potassa, arsenite of potassa is formed and hydrogen is liberated. It is not soluble in strong hydrochloric acid: but it is rapidly oxidized and converted into arsenic acid by nitric and nitrohydrochloric acids. Diluted nitric acid transforms it into arsenious acid. It combines directly with chlorine, iodine, bromine, and other elementary bodies. It is rapidly oxidized by an ozonized atmosphere, and is converted into arsenic acid (p. 102). When heated in a close tube, it sublimes unchanged: but when heated in air, it is oxidized and converted into arsenious acid, which is deposited in octahedral crystals.

Native arsenic usually occurs in rounded masses, or nodules, of a foliated lamellar texture, and is often associated with the ores of silver, cobalt, lead and nickel. Its color in the fresh fracture is nearly tin-white, but it speedily tarnishes.

ARSENIC AND OXYGEN.—There are two compounds of arsenic and oxygen, namely, arsenious acid and arsenic acid.

ARSENIOUS ACID (AsO_3); *White Arsenic; White Oxide of Arsenic.*—This is the best known, and most commonly occurring compound of arsenic. It is formed by the combustion of the metal; but is generally procured by the joint action of heat and air on certain arseniferous ores. Arsenious acid occurs in white translucent vitreous masses, often of a slight buff tint, and occasionally transparent, especially when first removed from the subliming vessel: on breaking the more opaque pieces, a translucent glassy nucleus is often found within them. When slowly sublimed in a current of air, as in a tube open at both ends, the vapor condenses in regular octahedral crystals; but if rapidly sublimed it forms a white powder, which, however, under the microscope, is evidently crystalline. The massive arsenious acid of commerce is generally pure, but when in powder it is sometimes adulterated with the sulphate of baryta or lime. The temperature at which arsenious acid rises in vapor is below that at which it fuses, and appears to be about 360°. The density of its vapor is 13·85, and it is inodorous. When heated under pressure, or when suddenly and highly heated, it fuses, and concretes on cooling into an amorphous vitreous solid. Arsenious acid is almost tasteless. In fine powder it has been described as having a rough or astringent taste. The specific gravity of the opaque arsenious acid is about 3·6, that of the transparent vitreous and fused acid is about 3·8. The solubility of arsenious acid in water has been variously stated, and it appears in some measure to be dependent upon its isomeric modifications; 100 parts of water at 60 dissolving 0·96 of the vitreous, and 1·25 of the opaque acid; and at 212°, 9·68 of the former and 11·47 of the latter. When these solutions are cooled down to 60°, 1·78 of the vitreous and 2·9 of the opaque are retained.

We have found by experiment that hot water cooling from 212° on the opaque variety in fine powder, does not dissolve more than 1-400th part of its weight. Water boiled for an hour and allowed to cool, will hold dissolved 1-40th part of its weight, or twelve grains to an ounce. If boiled for a shorter time not more than 1-80th part is retained in the cold solution. Cold water does not dissolve more than from 1-400th to 1-1000th of its weight. When mixed with water the powder partly floats, forming a film on the surface. A saturated solution of arsenious acid has a slightly acid reaction on litmus-paper. It is dissolved by alcohol and oils, but only to a slight extent. When a concentrated solution of the vitreous acid in boiling hydrochloric acid is suffered to cool, the crystals which it deposits have the properties of the opaque acid, and this transition from the one allotropic modification to the other is attended by the evolution of light; but if the opaque acid is used, or if the deposited crystals are redissolved, those which are subsequently deposited from the hydrochloric solution are formed without any luminous appearance.

Arsenious acid is decomposed at a dull red heat by hydrogen, and many of the metals. Its aqueous solution is rendered yellow by a current of sulphuretted hydrogen, and when the solution is acidulated by hydrochloric acid a yellow precipitate of tersulphide of arsenic falls; $AsO_3,+3HS=AsS_3+3HO$: a yellow tint is observed, even when only a 10,000th part of arsenious acid is dissolved. Hydrosulphate of ammonia does not precipitate a solution of arsenious acid unless an acid is added, when the tersulphide falls. Sulphate of copper and nitrate of silver give no precipitates in the solution until an alkali is added, when the former produces a green, and the latter a yellow precipitate. For the further action of tests upon this compound in the solid as well as in the dissolved state, *see* page 443.

Hydrochloric acid is a powerful solvent of arsenious acid, but by the continued application of heat much of the arsenic escapes as chloride. A copper wire introduced into this acid solution, moderately heated, is instantly coated with a layer of metallic arsenic of an iron-gray color. ($AsO_3+3HCl+3Cu=As+3HO+3CuCl$). On this reaction *Reinsch's process* for the detection of arsenic is based (page 444). When placed in contact with nascent hydrogen, as by adding zinc to the hydrochloric acid solution, or any soluble compound of arsenic to zinc and sulphuric acid, water and arsenuretted hydrogen are produced ($AsO_3+6H=AsH_3+3HO$). On this reaction, *Marsh's process* for the separation of arsenic is founded (page 444). Unlike antimony, the metal is not separated from its solutions by tin. Thus a strip of *pure* tin-foil, placed in a solution of arsenious acid containing one-tenth of its volume of hydrochloric acid, remains untarnished: no metallic arsenic is deposited. In a solution containing antimony, this metal under similar circumstances is rapidly separated in the cold, and is deposited on the tin in the form of a black powder. A boiling solution of potassa readily dissolves arsenious acid without change. If a strong alkaline solution is employed in excess, and pure zinc is added to the liquid, arsenuretted hydrogen escapes ($KO+6Zn+3HO+AsO_3=AsH_3+KO,6ZnO$). Fleitmann has recommended this process for the detection of arsenious acid when mixed with organic matter.

When arsenious acid is mixed with rather more than its bulk of dry acetate of potassa or soda, and the mixture is strongly heated in a closed tube, it undergoes fusion, a portion of metallic arsenic is sublimed, and the oxide of the compound radical *cacodyle*, recognized by its offensive odor, is set free ($2C_4H_3O_3+AsO_3=C_4H_6O,As+4CO_2$). It is decomposed by carbon and all carbonaceous fluxes, the metal being volatilized ($AsO_3+3C=As+3CO$). The cyanide of potassium, mixed with a little carbonate of soda to prevent fusion, and the ferrocyanide of potassium, heated with arsenious acid, decompose it, and metallic arsenic is sublimed: $2AsO_3+3KCy=2As+3KO,CyO$. Arsenious acid operates as a deoxidizer. When boiled with a solution of chromate of potassa, green oxide of chromium is produced. It decolorizes a solution of permanganate of potassa, reduces chloride of gold to the metallic state, and reduces the black oxide of copper to red oxide, when a few drops of the sulphate are added to a solution of arsenious acid in caustic potassa, and the liquid is boiled.

Chlorine, or a mixture of hydrochloric acid with chlorate of potassa, as well as an alkaline nitrate or chlorate, by fusion, convert it into arsenic acid and arsenate of potassa.

Traces of arsenious acid are not unfrequent in various chemical and pharmaceutical preparations: it has been detected in sulphuric, hydrochloric, nitric, acetic, and phosphoric acids, in phosphate of soda, and in emetic tartar. The preparations of bismuth and copper frequently contain it; and it is not unfrequently found associated with the hydrated oxide of iron, in the ochreous sediments of spring and river waters (page 138). This acid is used in many of the arts, especially in color-making, dyeing, and calico-printing; it is also used in medicine, and in a variety of preparations for the destruction of vermin. It is much employed in the steeping of seed-corn for the purpose of destroying the spores of fungi. In the small quantities in which it is commonly sold to the public it is directed to be colored with indigo of soot, a circumstance which must be borne in mind in searching for it in cases of poisoning. It is a powerful irritant poison, and has destroyed the life of an adult in the small dose of two grains. It is rapidly absorbed into the blood, and is equally fatal whether it is taken by the mouth or applied to a wound.

Arsenites.—These salts, when strongly heated, either evolve arsenious acid or metallic arsenic: in the latter case they are converted into *arsenates;* thus, $5(AsO_3)=3(AsO_5)+2As$: when heated with charcoal, or cyanide of potassium, metallic arsenic sublimes. The alkaline arsenites, when in solution, are decomposed by lime and the salts of lime, and a white precipitate of *arsenite of lime* falls, $2(CaO)AsO_3$: they are precipitated green by solutions of copper, $2(CuO)AsO_3$, and yellow by nitrate of silver, $2(AgO)AsO_3$. They are not precipitated by sulphuretted hydrogen, except when an excess of a stronger acid is present: in this way the hydrochloric solutions of those arsenites, which are insoluble in water, may also be decomposed. The *arsenites of ammonia, potassa,* and *soda,* are easily soluble, but are uncrystallizable: they are formed by dissolving the acid in the respective alkaline solutions. The supposed crystals of arsenite of ammonia deposited by the solution of arsenious acid in ammonia are quite destitute of ammonia, and consist only of arsenious acid. When arsenious acid is dissolved in the alkaline carbonates, it is deposited unaltered by evaporating the solution, so that it has been doubted whether this acid expels carbonic acid in the humid way.

The *arsenites* of *lime, baryta, strontia,* and *magnesia,* are with difficulty soluble in water, but readily soluble in hydrochloric acid: there are two arsenites of lime—one basic, $=2(CaO)AsO_3$; the other neutral, CaO,AsO_3. *Arsenite of potassa* is the active ingredient in the *Liquor arsenicalis* of the *Pharmacopœia*, and in *Fowler's mineral solution*, or *tasteless ague-drop.* A mixture of arsenious acid with carbonate of potassa, or soft-soap, is used as a wash for killing the fly in sheep. Another mixture, used by naturalists for preserving animals, consists of 32 parts of white soap, 32 of arsenious acid, 12 of dried carbonate of potassa, and 4 of powdered quicklime, with 1 part of camphor. Arsenuretted hydrogen is said to be slowly evolved from this composition.

Arsenite of Copper, $2(CuO)AsO_3$, *Scheele's green;* Aceto-Arsenite of Copper, *Schweinfürth green* $3(CuO,AsO_3)+(CuO,C_4H_3O_3)$ are green pigments much used in the arts. The latter, known also by the name of *Emerald green,* from its rich green color, containing 59 per cent. of arsenious acid. It is much employed in the coloring of paper-hangings and various articles of dress, as well as in the coloring of confectionery. When an alkaline arsenite is mixed with a solution of sulphate of copper, a precipitate of an apple-green color falls (*Scheele's green*), used as a pigment: it is prepared by dissolving 2 parts of sulphate of copper in 44 of hot water, and gradually adding it to a solution of 2 parts of carbonate of potassa and 1 of arsenious acid in 44 of hot water, the whole being well stirred during mixture: the arsenite of copper, in the form of a fine green powder, is gradually deposited, and is to be washed and dried at 212°. A similar preparation, known under the name of *Schweinfürth green,* is made as follows: 50 lbs. of sulphate of copper and 10 of lime are dissolved in 20 gallons of vinegar, and a boiling-hot aqueous solution of 50 lbs. of arsenious acid quickly stirred into it; the precipitate is dried and reduced to a fine powder. This green pigment, by reason of its being very loosely laid on paper-hangings is liable to be diffused in the air of a room, and under these circumstances it has in some cases given rise to the usual well-marked symptoms of chronic poisoning. Its employment on articles of dress and confectionery has been attended with more serious consequences. The following is a simple method of detecting arsenic in the colored substance. Cover a portion of the green paper with a solution of ammonia. The green pigment is dissolved and forms a blue solution with the ammonia, owing to the oxide of copper with which the arsenic is combined. Place a few crystals of nitrate of silver in a porcelain capsule, and pour upon them a few drops of ammoniacal solution. If arsenic is present, the crystals will acquire a superficial yellow color by the production of yellow arsenite of silver (*see* page 443). A small portion of the green powder, when heated in a reduction-tube, yields a sublimate of octahedral crystals, which may be easily identified as arsenious acid.

In the solutions of lead, antimony, and bismuth, arsenite of potassa forms white precipitates; added to nitrate of cobalt, it forms a pink precipitate; and bright yellow, with nitrate of uranium. With nitrate of silver it forms a yellow precipitate, very soluble in ammonia. All these precipitates are probably *arsenites* of the respective metals, and, heated by a blowpipe on charcoal, they exhale the smell of arsenic. They are decomposed when boiled in solution of carbonate of potassa or of soda; they are mostly soluble in an excess of arsenious acid, and are readily dissolved by nitric acid, and such other acids as form soluble compounds with their bases. *Native arsenite of lead* is found in France, Spain, and Siberia, and the mineral called *Condurrite* appears to be an *arsenite of copper.*

ARSENIC ACID (AsO_5) is obtained by distilling a mixture of 1 part of hydrochloric, 12 parts of nitric, and 4 parts of arsenious acid: nitric oxide gas is given off, and when the contents of the retort have acquired the consistency of a thin syrup, they are poured into a porcelain dish, and evaporated by a moderate heat; suddenly, the arsenic acid (which is anhydrous) concretes into an opaque white mass, which should be put, whilst warm, into a well-stopped phial. The hydrochloric acid is only useful in promoting the solution of the white arsenic, which otherwise adheres to the retort, and occasions irregular ebullition.

Arsenic acid is a white deliquescent compound; it forms several crystallizable hydrates: it fuses in close vessels at a heat approaching to redness, and concretes on cooling into a vitreous mass; at a higher temperature it is decomposed, oxygen is evolved, and arsenious acid sublimes ($AsO_5=AsO_3+2O$). Its specific gravity is about 3·7. It requires for solution 6 parts of cold and 2 of boiling water; its solution reddens vegetable blues, and has an acid and metallic taste. When water is poured upon the solid acid, part only is immediately dissolved, and another portion, as is the case with phosphoric acid, remains undissolved, but after a time, upon agitating the solution, the whole is taken up. Arsenic acid gives with lime-water a white precipitate, and with ammonio-sulphate of copper a pale greenish-blue precipitate. It is converted by sulphurous acid into arsenious acid, and by the bisulphite or hyposulphite of soda into arsenite of soda ($AsO_5+2SO_2=AsO_3+2SO_3$). It exerts no reducing action on chloride of gold, permanganate of potassa, or the salts of copper and chromium. With aniline it produces a purple dye. When heated with hydrochloric acid, and copper is introduced into the liquid, metallic arsenic is only slowly deposited; and there is no deposit unless the arsenic acid is in comparatively large proportion. Sulphuretted hydrogen very slowly affects it, and throws down after a time a pale yellow pentasulphide ($AsO_5+5HS=AsS_5+HO$). To effect its complete precipitation, it should be first converted into arsenious acid by warming the solution with sulphurous acid. Another method consists in acidulating the liquid with hydrochloric acid, then adding a solution of hyposulphite of soda, and boiling the mixture. Tersulphide of arsenic is precipitated (AsS_3). With nitrate as well as with the ammonio-nitrate of silver, arsenic acid gives at once a red-brown precipitate. It is decomposed by nascent hydrogen like arsenious acid, and yields arsenuretted hydrogen. When the solid acid is heated to redness with carbon or cyanide of potassium, the arsenic is reduced to the metallic state, and is sublimed.

ARSENATES are produced by the union of this acid with metallic oxides; those which are insoluble may be formed by adding arsenate of potassa to their respective solutions. The normal arsenates are constituted like the phosphates, of 1 atom of acid with 3 of base, and there are also salts with 1 and 2 atoms of basic oxide, in which the deficient base is replaced by 1 and 2 atoms of water; but there appear to be no modifications corresponding to the pyrophosphates and metaphosphates. The arsenates which are insoluble in water, are soluble in dilute nitric acid and in such other acids as do not form insoluble compounds with their bases: ammonia precipitates them from these solutions. They are readily decomposed by charcoal at a red heat; but many of them, when heated alone, are unchanged even at a higher temperature. They are decomposed when boiled in solutions of the fixed alkaline carbonates. The *soluble arsenates* generally give a white precipitate with lime-water $2(CaO)HO,AsO_5$; they are not immediately precipitated by a solution of sulphuretted hydrogen: with protosulphate of iron they give a white precipitate (or yellowish if arsenious acid be at the same time present). They give white precipitates with solutions of lead and zinc; yellow with the persalts of uranium and mercury; red with the solutions of salts of cobalt; green with those of nickel; pale greenish-blue with those of copper $2(CuO)HO,AsO_5$, and reddish-brown with those of silver $3(AgO)AsO_5$. The last reaction is the most characteristic; hence nitrate of silver is alone sufficient for the detection of an arsenate. These precipitates are mostly soluble in hydrochloric acid, and in solutions of ammoniacal salts. Arsenate of potassa gives a yellow precipitate with persulphate of uranium when the solution is so diluted as to contain only a 10,000th part of arsenic acid; and with protosulphate of iron a white cloud is perceptible under the same state of dilution. All the arsenates, when dissolved in water or in dilute nitric acid, give a white precipitate with acetate of lead, which fuses and emits arsenical fumes when heated on charcoal before the blowpipe.

The salt commonly called *Binarsenate of potassa* $=KO,AsO_5$, may be formed either by adding excess of arsenic acid to a solution of potassa, and evaporating; or by heating to redness, in a Florence flask, a mixture of equal parts of nitre and white arsenic. During the latter operation much nitrous gas is evolved, and on dissolving the residue in water, filtering, and evaporating, prismatic crystals are obtained, resembling those of the corresponding phosphates of ammonia and potassa; they are soluble in 5·3 parts of water at 40°, and insoluble in alcohol; their formula is $KO,2(HO),AsO_5$. Macquer was the first who procured this salt; hence it is termed *Macquer's Arsenical salt.* It is not easily decomposed by heat alone, and may be fused and kept red-hot without undergoing other change than losing a little water; but when mixed with about an eighth of charcoal-powder and distilled, metallic arsenic rises, and carbonate of potassa, mixed with a part of the charcoal, remains in the body of the retort. This salt as well as the arsenite, is used in medicine. It is a delicate test of the presence of silver, in solutions of which it occasions a red-brown precipitate; it is also sometimes used to separate iron from manganese; it produces in the persalts of iron a white precipitate, whilst the arsenate of manganese remains in solution. *Arsenate of soda* is extensively used in calico-printing. When dissolved in water and mixed with sugar, it is sometimes employed as a fly-poison. Paper impregnated with this liquid, and dried, is sold under the name of *Papier Moure.* The arsenates of the alkaline earths are not soluble in water. When a solution of an arsenate is acidulated with hydrochloric acid, and boiled with hyposulphite of soda, tersulphide of arsenic is precipitated. (*See* p. 437.)

Arsenic acid forms a nearly insoluble compound salt with ammonia and magnesia, resembling the ammonio-magnesian phosphate. When phosphoric acid or a phosphate is not present, arsenic may be thus separated, and its quantity determined. If a solution of sulphate of magnesia is mixed with a solution of arsenic acid; and if ammonia, with chloride of ammonium, is then added, an insoluble crystalline precipitate of arsenate of ammonia and magnesia is slowly produced. This is not only a test for arsenic acid, but it serves to distinguish it from arsenious acid, as this forms no similar compound salt. The precipitate, when dried at 212°, has the composition $NH_3,HO,2(MgO)AsO_5,HO$. It contains 62·9 per cent. of arsenic acid. It does not, like the corresponding phosphate, admit of calcination, as a portion of arsenic would be expelled at a high temperature.

ARSENATES OF IRON.—The protosalts of iron give a white precipitate with arsenate of ammonia, which gradually becomes green on exposure to air; it appears from Chenevix's analysis to be $3(FeO),AsO_5,6HO$. When solutions of perchloride of iron and bibasic arsenate of soda are mixed, a white *perarsenate of iron* falls: $2Fe_2Cl_3+3[2NaO,AsO_5]=2Fe_2O_3,3AsO_5+6NaCl$. This salt, when dried at common temperatures, retains about 18 per cent. of water (=12 atoms) which it loses when heated, and becomes red, and at higher temperatures it glows and acquires a yellow color. It is insoluble in water; hence hydrated peroxide of iron has been used as a chemical antidote in poisoning by arsenic. This oxide precipitates both arsenious and arsenic acid when these are in *solution* in water. The arsenates of the other metallic oxides call for no special notice.

ARSENIC AND HYDROGEN; ARSENURETTED HYDROGEN GAS.—*Hydride of Arsenic* (AsH_3).—When nascent hydrogen comes into contact with arsenic, or any of its soluble compounds, a portion of the metal is carried over in a state of combination with the hydrogen. When arsenious acid is added to dilute sulphuric acid, and zinc is dissolved in the mixture, the liberated hydrogen is rich in arsenic; but free hydrogen is also evolved. Pure arsenuretted hydrogen is best obtained by the action of hydrochloric acid upon a pulverized alloy of zinc and arsenic, obtained by fusing together equal parts of these metals.

This gas is colorless: it has a nauseous odor resembling garlic, and is so poisonous that extreme caution must be observed in dealing with it. It has proved fatal to three chemists, who were engaged in experiments upon it. The gas blackens paper impregnated with nitrate of silver, but it produces no change of color on paper impregnated with a salt of lead.

Arsenuretted hydrogen may be collected and retained over water, which, however, absorbs it to the amount of about one-fifth of its volume, and, if it contain air, a dark-colored film of arsenic is gradually deposited; it is not absorbed by alkaline solutions, nor by alcohol or ether, but oil of turpentine absorbs it largely. It is liquefied, under atmospheric pressure, when cooled down to —40°. Faraday could not solidify it at 166° below 0°. Arsenuretted hydrogen is decomposed at a full red heat, arsenic is deposited, and 2 volumes of the gas afford 3 volumes of hydrogen. When mixed with an insufficient quantity of air or oxygen for its perfect combustion it deposits metallic arsenic in burning; but with excess of oxygen it explodes with violence, and forms water and arsenious acid. It burns in contact with air with a pale blue flame, forming water and arsenious acid, and depositing arsenious acid upon the sides of the jar as the flame descends ($AsH_3+6O=3HO+AsO_3$). These are the products of its combustion when burnt from a jet. If a clean glass plate, or a surface of porcelain, is held above the point of the flame, arsenious acid and water only are deposited; if held so as to bisect the flame a deposit is obtained, consisting of metallic arsenic in the centre, and of white arsenious acid at the circumference. When deposited on glass the central portion is opaque if viewed by transmitted light, but by reflected light it has a strong metallic lustre. The deposit is of a hair-brown color at the circumference. It possesses the following additional chemical characters: 1. It is entirely dissolved by fuming nitric acid, and leaves, on evaporation, arsenic acid. 2. It is readily dissolved by a fresh solution of chloride of lime, and leaves, on evaporation, some arsenate of lime mixed with chloride. 3. It is not readily dissolved by hydrosulphate of ammonia; on evaporation it leaves a yellow residue of sulphide of arsenic. The antimonuretted hydrogen, produced under similar circumstances, has widely different properties. In addition to those elsewhere described (page 428) the following may be noticed in contrast with the characters of an arsenical deposit: 1. It is not dissolved by a solution of chloride of lime. 2. It is readily dissolved by hydrosulphate of ammonia, leaving, on evaporation, an orange-red sulphide of antimony.

The sp. gr. of arsenic in vapor is 10·39, and the sp. gr. of arsenuretted hydrogen is 2·695. As in the analogous compound of phosphorus—half a volume of the vapor of arsenic=75, is combined with three volumes of hydrogen=3, the $3\frac{1}{2}$ volumes being condensed into 2 volumes of the gas (pp. 66 and 229).

	Atoms.	Equiv.	Per cent.	Vol.	Sp. Gr.
Arsenic	1	75	96·15	$\frac{1}{2}$	5·195
Hydrogen	3	3	3·85	3	0·207
	1	78	100·00	2	5·402

The sum of the sp. gr. of the constituents, divided by 2(5·402÷2), is equal to 2·701, which is but little in excess of the sp. gr. determined by Dumas. Compared with hydrogen, the sp. gr. is one-half of the equivalent weight, namely, 39. The observation occurs with this as with respect to the phosphorus-compound: one volume of the vapor of arsenic is equivalent to two atoms of this elementary substance.

Arsenuretted hydrogen gas is instantly decomposed by chlorine; and if chlorine is suffered to ascend into a jar containing it, while standing over water, each bubble inflames, producing hydrochloric acid, while brown fumes of arsenic are produced and deposited; if the arsenuretted hydrogen is sent up in the same way into chlorine, when this gas is in great excess hydrochloric and arsenious acids are immediately formed. The gas is similarly decomposed by iodine and bromine. Agitated with a solution of sulphate of copper, the gas is absorbed, and arsenide of copper and water are formed. $3(CuO,SO_3)+AsH_3=Cu_3As+3HO+3SO_3$. This action furnishes a means of testing the purity of the gas, for any uncombined hydrogen remains unabsorbed. It reduces the salts of silver, gold, platinum, and rhodium, to the metallic state, and arsenious acid remains in solution: thus, with nitrate of silver, the results are silver, arsenious acid, water, and nitric acid. $6(AgO,NO_5)+AsH_3=6Ag+AsO_3+3HO+6NO_5$. We find by experiment that there are no liquids which so completely arrest and decompose this gas as a saturated solution of nitrate of silver and fuming nitric acid.

ARSENIC AND CHLORINE; TERCHLORIDE OF ARSENIC ($AsCl_3$).—This compound may be formed: 1. By throwing finely-powdered arsenic into chlorine; the metal burns and produces a volatile liquid; or by passing dry chlorine over arsenic placed in a tube, and gently heated: the resulting vapor of the chloride should be condensed in a receiver cooled by ice, and may be purified by redistilling it with a little powdered arsenic. 2. Distil 6 parts of corrosive sublimate with 1 of powdered arsenic; the chloride passes into the receiver in the form of an unctuous fluid, formerly called *butter of arsenic.* 3. 1 part of arsenious acid with 10 parts of sulphuric acid, are put into a tubulated retort, and the temperature raised to about 212°. Fragments of fused common salt are then thrown in by the tubulature; by continuing the heat, and successively adding the salt, chloride of arsenic is obtained; it distils over, and may be condensed in cold vessels. Very little hydrochloric acid is disengaged, but towards the end of the operation, a portion of hydrated chloride of arsenic is produced, which floats upon the pure chloride, and appears more viscid and colorless. Mixed with a large quantity of water, the chloride of arsenic is decomposed, and arsenious acid is formed, hydrochloric acid being at the same time produced. On this reaction Schneider, in 1852, founded a process for procuring arsenic by distillation in cases of poisoning. When fused chloride of sodium is employed, this should always be kept in excess, as if the sulphuric acid is in excess, the arsenious acid will be retained by it in the retort. If the mixture of arsenious and hydrochloric acids is saturated with chlorine, or chlorate of potassa, the arsenic is converted into arsenic acid, and barely a trace passes over as chloride.

Chloride of arsenic, when concentrated, is a dense oleaginous transparent liquid: it does not freeze at 0°; it boils at about 270°, the density of its vapor being 6·3: it exhales vapor when exposed at common temperatures to the air. With a small quantity of water it forms what has been termed *hydrated chloride of arsenic:* this is probably a hydrochloric solution of arsenious acid; [$AsCl_3+3HO=AsO_3+3HCl$], and when more largely diluted, arsenious acid is deposited; but when a solution of arsenious acid in excess of hydrochloric acid is heated, the whole volatilizes, and there is no residue; so that when hydrochloric acid containing arsenious acid is distilled, the product which passes over is always arseniferous; and when any arseniferous acid acts upon common salt, the hydrochloric acid which is evolved carries arsenic with it. On this reaction is based a method of separating arsenic from mineral and organic substances (*see* page 444). A diluted solution of chloride of arsenic reduces a solution of gold to the metallic state. When heated with metallic copper, arsenic is deposited on the metal; and when a rod of zinc is introduced into the liquid, the arsenic rapidly escapes as arsenuretted hydrogen.

There is no pentachloride of arsenic; *i. e.*, no chloride corresponding to arsenic acid. When arsenic acid is distilled with hydrochloric acid, terchloride only appears to be produced to a limited extent. The greater part of the arsenic acid remains unchanged in the retort.

A solution of the chloride of arsenic is used in medicine. It is a powerful poison, as it is readily absorbed. A quantity equivalent to the tenth part of a grain has produced serious symptoms.

ARSENIC AND SULPHUR. BISULPHIDE OF ARSENIC.—*Red sulphide of Arsenic. Realgar* (AsS_2).—By slowly fusing a mixture of metallic arsenic and sulphur, or by heating 15 parts of arsenious acid with 8 parts of sulphur, a *red sulphide of arsenic* is obtained. It is crystallizable, and of a vitreous fracture: its specific gravity is 3·4 to 3·5. It is easily fusible, and may be sublimed, unaltered, in close vessels. It is usually known under the name of *Realgar*, and occurs *native.* It is used in the preparation of the pyrotechnical compound, called *White Indian Fire*, which consists of 24 parts of saltpetre, 7 of sulphur, and 2 of realgar, finely powdered and well mixed. The mixture burns with a splendid white flame of great brilliancy.

TERSULPHIDE OF ARSENIC. *Orpiment. Sulpharsenious Acid* (AsS_3).—When sulphuretted hydrogen is passed through a solution of arsenious acid in dilute hydrochloric acid, this sulphide is formed. It is also procured by subliming a mixture of sulphur and arsenious acid, or arsenic, in proper proportions. It is fusible, and sublimes in close vessels without change: it has a rich golden-yellow color, and assumes a lamellar texture on cooling. Heated in air, it burns with a pale-blue flame, producing fumes of sulphurous and arsenious acids. Its specific gravity is 3·45. It is soluble in caustic alkaline solutions; it is insoluble in diluted acids, but is decomposed by nitric and nitro-hydrochloric acids, forming arsenic and sulphuric acids. These sulphides are decomposed by fusion with potassa; sulphide of potassium and metallic arsenic in the form of a sublimate, are the results.

As this sulphide is commonly met with, it contains undecomposed arsenious acid in variable proportions. This may be separated by boiling the compound in water, in which the sulphide is insoluble. Although the sulphide is not very soluble in strong hydrochloric acid, yet under continued heat, chloride of arsenic and arsenuretted hydrogen are produced. It is only the hydrated precipitated sulphide that is readily dissolved by strong solutions of potassa, soda, or ammonia. By its solubility in ammonia sulphide of arsenic may be separated from sulphide of antimony. For the complete reduction of this sulphide, Otto recommends that it should be heated with ten parts of a mixture consisting of 1 part of cyanide of potassium, and 3 parts of carbonate of soda, finely-powdered and well-dried: sulphocyanide of potassium is formed and metallic arsenic is sublimed ($2AsS_3+3KCy=3KCyS_2+2As$).

An ammoniacal solution of this sulphide has been employed as a dye-stuff. Orpiment is the basis of a pigment called *King's Yellow*. *Native Orpiment* (the *auripigmentum* of the ancients) is of a bright lemon or golden color. It is generally massive and lamellar. This, and the preceding sulphide, act as sulphur acids, and form salts (*Arsenio-sulphides*), with sulphur bases.

PERSULPHIDE OF ARSENIC. *Sulpharsenic Acid* (AsS_5).—When sulphuretted hydrogen is passed through a concentrated solution of arsenic acid, a pale yellow precipitate very slowly falls, which may be sublimed, without change, in close vessels. It is fusible, and soluble in alkaline solutions, but insoluble in boiling water. The same compound is obtained when sulphuretted hydrogen is passed through a concentrated solution of arsenate of potassa, and the resulting sulpho-salt is decomposed by hydrochloric acid (p. 437). This compound reddens litmus-paper. Its reactions are those of a sulphur acid. Thus, it combines with alkaline and metallic sulphides to form sulphur salts, and it expels carbonic acid from the carbonates. The sulphides of arsenic are poisonous, but in a less degree than arsenious acid. Common orpiment, owing to its containing arsenious acid, is a virulent poison.

There is a native sulphide of arsenic and iron diffused with ordinary pyrites ($FeAs,FeS_2$). It is of a more silvery color than common pyrites. When heated, it exhales an odor of arsenic. It is called arsenical pyrites, or *mispickel*. It is an abundant source of arsenious acid. By the decomposition of arsenical pyrites, under exposure to air and moisture, insoluble compounds of the acids of arsenic and oxide of iron are diffused through certain soils, and are contained in the sediments of spring and river waters.

ALLOYS OF ARSENIC; ARSENIDES.—Arsenic unites with most of the metals, forming compounds which are generally brittle and comparatively fusible. Arsenic and *iron* form compounds which are more brittle, hard, and fusible than iron: iron containing only 2 or 3 per cent. of arsenic becomes very brittle when heated. *Native arsenide of cobalt* occurs in cubic, octahedral, and dodecahedral crystals, sp. gr. 6·78, of a tin white color; it contains about 20 per cent. of cobalt and 80 of arsenic, and is therefore Co_2As_3. The ore known in Germany as *speiskobalt* is an arsenide of cobalt, iron, and nickel. Arsenide of *nickel* is gray and brittle. *Kupfernickel* is a *native arsenide*=$AsNi_2$; and the white arsenical nickel, or *nickel pyrites*, is AsNi. When *copper* is heated to redness with excess of arsenic, a gray arsenide is formed; it has been called *white tombac.* Arsenide of *lead* is obtained by heating lead with excess of arsenic or of arsenious acid; it is of a gray, crystalline, brittle compound. A very minute quantity of arsenic (less than 1 per cent.) is always contained in common lead shot; it gives the lead the property of spherical granulation when the fused metal is passed through a sieve and suffered to fall through the air till it solidifies. Arsenide of *antimony* is brittle, hard, and very fusible: it occurs *native*, containing about 36 per cent. of antimony; this ore therefore is $SbAs_3$.

TESTS FOR ARSENIC; ANALYSIS IN CASES OF POISONING.—*Arsenious acid*, or *arsenic*, as it is commonly called, is a white crystalline powder. 1. When heated on platinum foil, or mica, it is entirely volatile at a moderate heat, without undergoing fusion. It escapes in a white smoke, which has no odor. 2. When gently heated in a small reduction-tube, closed at one end, it sublimes without fusing, in well-defined transparent octahedral crystals, or derivatives of the octahedron, sometimes visible without the aid of a microscope. 3. A small portion on a loop of platinum-wire introduced into a Bunsen's jet, burns with a pale blue flame, emitting dense white fumes. 4. When a solution of hydrosulphate of ammonia is poured upon the powder it undergoes no immediate change of color; but by exposure to heat, or by spontaneous evaporation of the liquid, it is converted into an orange-yellow sulphide of arsenic, which is dissolved by ammonia, but not by hydrochloric acid. 5. The powder is not easily dissolved by water, even at a boiling temperature. It is, however, readily dissolved by potassa without change, and by hydrochloric acid which converts it into volatile chloride of arsenic. A small quantity of hydrochloric acid in water renders arsenious acid much more soluble. 6. When heated with 3 or 4 parts of soda-flux (prepared by calcining acetate of soda in a close platinum-crucible) it yields a dark iron-gray sublimate of metallic arsenic. In the absence of soda-flux, powdered ferrocyanide of potassium may be used as a reducing agent. The sublimate of metallic arsenic may be identified by the following characters. When the glass with the metal is gently heated in a larger tube, the metal is oxidized and volatilized in the form of a white crystalline sublimate of arsenious acid. When treated with strong nitric acid containing nitrous acid, and evaporated to dryness, it leaves a residue of arsenic acid, which is known by the brick-red color, or stain produced on the addition of a few drops of nitrate of silver. Cadmium, tellurium, selenium, and mercury produce sublimates; but when heated, or acted on, by nitric acid, the results are wholly different.

A *solution* of arsenious acid in water is tasteless, and feebly acid to litmus-paper. 1. Ammonio-nitrate of silver produces with it a yellow precipitate of arsenite of silver. 2. Ammonio-sulphate of copper gives a green precipitate. This precipitate, when collected, dried, and heated in a tube, yields a sublimate of arsenious acid in octahedral crystals. The green precipitate, dissolved in a few drops of solution of ammonia, and treated with a crystal of nitrate of silver, produces on the surface of the crystal a layer of yellow arsenite of silver. 3. A current of sulphuretted hydrogen produces a yellow precipitate, which is completely thrown down on acidulating the liquid with a few drops of diluted hydrochloric acid. This yellow precipitate (sulphide of arsenic) is known from all others of a similar color. 1. By its insolubility in hydrochloric acid; 2. By its dissolving in ammonia, forming a pale colorless solution; and 3. By its yielding a sublimate of metallic arsenic when heated with 2 or 3 parts of powdered ferrocyanide of potassium.

Arsenic acid.—This compound is easily recognized. 1. By its fixedness when heated. 2. By its great solubility in water, and the strong acid reaction which it imparts to water. 3. By the color of the precipitate given by a solution of nitrate or ammonio-nitrate of silver. When the arsenic acid is in a very dilute state, the precipitate is of a pale brownish color, becoming of a deeper and browner red in proportion to the quantity present. Metallic arsenic and arsenious acid may be readily identified by these properties when converted into arsenic acid by the action of fuming nitric acid.

When arsenic is contained in *organic liquids* it may sometimes be separated in lumps, or powder, by washing; or if dissolved, it may be precipitated as sulphide by sulphuretted hydrogen, and this may be tested in the manner above described. *Reinsch's process* furnishes a useful trial test under these circumstances. The suspected liquid, which should not contain nitric acid, or any chlorate or nitrate, must be acidulated with pure hydrochloric acid (its purity having been previously determined) in the proportion of 1 part of acid to 6 or 7 parts of the liquid. The acid liquid is then brought to the boiling point, and a piece of bright copper-wire, or foil (free from arsenic) is introduced. If the quantity of arsenic is minute, the copper will acquire a metallic deposit of a bluish or purple color, passing to gray or iron-gray, in proportion to the quantity of arsenic present. The coated copper, washed and dried, will, when heated in a small reduction tube, yield a sublimate of octahedral crystals of arsenious acid. If there is no tarnish or deposit on the copper after some minutes' boiling, it may be inferred that arsenic is either not present, or that the proportion is exceedingly small. On the other hand, there may be a deposit, but insufficient to yield crystals of arsenious acid. In this case the following process may be resorted to:

The solid or tissue, previously dried and divided into small portions, or an extract of the suspected liquid, may be placed in a flask or retort with a sufficient quantity of pure and concentrated hydrochloric acid to render the mass quite liquid. The receiver should contain a small quantity of distilled water. If a globular flask is used, this may be connected with the receiver by means of a long narrow tube, kept cool by wetted blotting-paper folded round it. The distillation should take place slowly, by means of a sand-bath, and be carried nearly to dryness. A distillate is thus obtained containing either the chloride of arsenic, or a mixture of hydrochloric and arsenious acids. If this is colored, or mixed with organic matter, it should be submitted to a second distillation. In some cases, as where the substance has not been thoroughly dried, a second distillation, with a fresh portion of hydrochloric acid, may be required to remove the whole of the arsenic; but with ordinary care this is not necessary. One-third of the liquid distillate (diluted with water if too acid) may now be heated with a small piece of polished copper foil (*Reinsch's process*, p. 435). If arsenic is present, even to the 1-4000th of a grain, the copper will indicate this by a change of color—the metallic lustre being retained. By using other portions of copper successively, the whole of the arsenic may be extracted. The remaining two-thirds of the liquid should then be submitted to *Marsh's process* with the following modifications. The distillate, if very acid, should be so diluted that its action on zinc may not be too violent. The most convenient form of apparatus is a tube, about an inch in width and six or eight inches in height, provided with a well-fitted cork, through which passes a safety-funnel tube on one side, and an exit or delivery-tube, bent at a right angle, on the other side. The exit-tube should be connected by corks with a short wide tube, containing fragments of fused chloride of calcium, for the purpose of drying the gas. To the other end of the drying-tube there should be fitted a long tube of hard glass (free from lead), about one-quarter of an inch in diameter, and provided with two or three capillary contractions. This tube should be bent at a right angle, so that the end of it may dip into a solution of nitrate of silver.

Pure zinc having been placed in the apparatus, the acid distillate is poured upon it through the funnel. After a short time, if arsenic is present, the bubbles of hydrogen, as they escape, will darken the solution of nitrate of silver. The liquid will first become of a pale brown color, gradually deepening to black, according to the amount of arsenic present (p. 435). When the silver solution has undergone this change, the horizontal glass tube may be heated to redness, about an inch before each capillary contraction. The arsenuretted hydrogen will be thereby decomposed, and a dark mirror of metallic arsenic, in the form of a ring, will be deposited in the contracted portion of the tube. By this arrangement, three or more metallic deposits of arsenic, corresponding to each contraction, may be procured.

When the gas has spent itself in the silver solution, this may be removed. The end of the delivery-tube should then be washed, and allowed to dip into a small quantity of fuming nitric acid containing nitrous acid. This completely arrests and decomposes the arsenuretted hydrogen.

The chemist has now before him all that is necessary to identify the substance as arsenic. The glass tube is detached from the apparatus, and the metallic sublimates are obtained separately by melting the glass in the contracted portions. One may be sealed up and preserved; one may be tested by applying a gentle heat to the metallic deposit, when a brilliant ring of colorless octahedral crystals may be obtained, plainly visible under the microscope. With respect to the other tube, the portion of glass containing the metallic deposit may be separated by a file, broken into fragments, and digested in a small porcelain capsule, in a few drops of fuming nitric acid. On evaporating to dryness and adding a solution of nitrate of silver, a reddish-colored precipitate, entirely soluble in ammonia, indicates that arsenic acid was present, and that the metallic deposit was arsenic. It is here assumed that the chemist is obliged to rely exclusively upon the results obtained by decomposing the arsenuretted hydrogen gas by heat. In general, however, it will be found that the silver solution and the nitric acid which have been employed to receive the surplus gas, will yield satisfactory evidence, and render a special analysis of the metallic deposits unnecessary.

1. The darkened solution of nitrate of silver is filtered, in order to separate the metallic silver. A slight excess of pure hydrochloric acid is added to the filtrate, in order to throw down completely any surplus silver contained in the liquid. When the chloride of silver has been deposited, the liquid should be again filtered, and a current of washed sulphuretted hydrogen passed into it. If the arsenic is in sufficient quantity, a golden-yellow precipitate of tersulphide of arsenic immediately appears. This will be found to have the properties elsewhere assigned to it (p. 441).

2. The fuming nitric acid into which the gas has been passed, may be evaporated to dryness on a sand-bath in a clean porcelain capsule. A white deliquescent acid residue is thus obtained. On adding to this residue a few drops of nitrate, or of ammonio-nitrate of silver, a brick-red precipitate of arsenate of silver is immediately produced. (For further details of this process see *Guy's Hospital Reports*, Oct. 1860, p. 253.)

The usual method of detecting arsenic in the tissues or organs of the body, consists in rendering the arsenic soluble in the midst of a large quantity of carbonized organic matter, which, in spite of every care, will more or less accompany it. By the process of distillation as originally suggested by Schneider, the arsenic is removed from the organic matter, and thus separated from a large number of metals which do not form volatile chlorides at a low temperature. The residue in the retort, after the complete separation of arsenic, may be analyzed for mercury, antimony, and other metals. This process does not interfere with the carbonization of the residue by sulphuric acid, if necessary. In the state of *chloride*, arsenic is distinguished from all metals excepting antimony, by its ready conversion into a gaseous hydride, and by the entire decomposition of this hydride by heat. Lastly, by means of the *hydrate* the arsenic may be reproduced, 1st, as metal; 2d, as arsenious acid; and 3d, as arsenic acid, beyond which it is unnecessary to carry the analysis. The processes of Marsh and Reinsch are not here resorted to until after the arsenic has been separated from other substances by distillation. These processes should corroborate each other; and the only caution required, is that pure zinc and copper, as well as pure hydrochloric and nitric acids, should be employed. These substances should each be separately tested in the apparatus on a sufficient scale, before the analysis is commenced.

In reference to *antimony*, there are characteristic differences, which have been already described (p. 434). The only method by which the *quantity* of arsenic can be approximately determined in these researches, is by condensing the whole of the arsenic obtained from a given weight of the material, in fuming nitric acid, and precipitating the arsenic so obtained as arsenate of ammonia and magnesia (p. 439). A hundred parts of this precipitate, dried at 212°, are equivalent to 54·14 of arsenious acid.

If the organic substance submitted to examination, should be in a state of putrefaction, sulphuretted hydrogen may be found in the distillate. This may be removed by the addition of chlorine, and heating the liquid. If the quantity is small, the sulphuretted hydrogen may be stopped by placing lead-paper in the first portion of the drying-tube. When sulphuretted hydrogen comes over with arsenuretted hydrogen, the metallic deposit, obtained by heating the current of gas, is, in part at least, converted into yellow sulphide of arsenic. If arsenic acid is present, this should be converted into arsenious acid by sulphurous acid before submitting it to distillation. If sulphide of arsenic or orpiment is present, this should be converted into arsenic acid by fuming nitric acid, and then submitted to distillation as above described. By the process above described, minute traces of arsenic have been separated from Thames mud, the ochreous deposits of rivers, and from the salts of copper as well as from animal solids and fluids in cases of poisoning.

CHAPTER XXXVII.

MERCURY ($Hg=100$).

THE principal ore of this metal is the *sulphide* or *native cinnabar*, from which mercury is separated by distillation, either with quick-lime or iron-filings, or by simply burning off the sulphur. Mercury occurs *native*, in small globules, generally dispersed through the sulphide. It is also found as a *chloride*, *iodide*, and *selenide*, but these are rare ores: in combination with silver it constitutes *native amalgam*.

Mercury is a brilliant silvery-white fluid-metal, whence the terms *hydrar-*

gyrum (ὕδωρ ἄργυρος) and *quicksilver*. It has been known from remote ages. It is liquid at all common temperatures, solid at —40°, and contracts at the moment of congelation. Its characters, when frozen, vary with the temperature, being flexible when verging towards liquefaction, but brittle at lower temperatures. It boils at about 660°. It emits vapor at all temperatures above 40°, but no apparent spontaneous evaporation goes on from it when below that temperature. Its sp. gr. at 60° is 13·56, but in the solid state it exceeds 14. The specific gravity of mercurial vapor is 6·976. When mercury is pure, it is not affected by agitation in contact with air; but when impure, it becomes covered with a gray powder, which is a mixture of the foreign metallic oxide and finely-divided mercury. When pure mercury is shaken with water, ether, sulphuric acid, or oil of turpentine, or rubbed with sugar, chalk, lard, conserve of roses, &c., it is reduced to a gray powder, which consists of minute mercurial globules, blended with the foreign body; and when this is abstracted they again unite into running mercury. In well-made mercurial ointment these globules are not discernible by the naked eye. The extent to which this division may be carried, is well illustrated in the preparation termed *precipitated mercury;* obtained by precipitating a solution of corrosive sublimate by protochloride of tin: the liberated mercury forms so fine a precipitate that it is perfectly black, and requires several hours to subside.

There are two oxides of mercury, both of them salifiable: a dioxide or suboxide, Hg_2O, and an oxide, HgO.

SUBOXIDE OF MERCURY. *Dioxide of Mercury; Black Oxide of Mercury; Mercurious Oxide* (Hg_2O).—This oxide (formerly termed *protoxide*) is obtained when finely levigated dichloride of mercury (calomel) is triturated with excess of lime-water; it must be carefully washed with cold water, and dried at common temperatures, under exclusion of light. It is a black or brownish-black powder, sp. gr. 10·6, easily resolved by light, or by heat into metal and oxide. The salts of this oxide are generally obtained either by its direct solution, or by digesting excess of mercury with the acids, or with the salts of the red oxide, or by double decomposition: they are usually yellow when basic, but otherwise colorless, soluble in water, redden litmus, and taste metallic; some of them are resolved by the action of water into an insoluble basic, and a soluble acid salt. They give black precipitates, with the caustic alkalies. With carbonate of potassa they afford a brownish-yellow, and with bicarbonate a yellowish-white precipitate, sparingly soluble in an excess of the bicarbonate, and becoming black and losing carbonic acid when boiled. With carbonate of ammonia the precipitate is at first white, but blackens on adding it in excess. With hydrochloric acid and soluble chlorides these salts give a white precipitate of subchloride of mercury, which is immediately blackened by the alkalies. With sulphuretted hydrogen, and the hydrosulphates, the precipitate is black; with phosphate of soda, white; with iodide of potassium, greenish-yellow, darkened by an excess of the precipitant; with hydrocyanic acid, mercury is precipitated, and a cyanide of mercury formed: $Hg_2O+HCy=Hg+HgCy+HO$.

OXIDE OF MERCURY.—*Red Oxide; Peroxide; Mercuric Oxide* (HgO).—This oxide is produced by heating mercury in a long-necked flask, open to the air, nearly to its boiling-point. It becomes slowly coated with reddish-brown scales and crystals, and is ultimately converted into a red crystalline substance, called in old pharmaceutical works, *precipitatum per se*, or *calcined mercury*. It may also be obtained by heating nitrate of mercury, so long as fumes of nitrous acid are evolved; the resulting oxide is in the form of an orange-red crystalline powder. This oxide is also thrown down in the form of a yellow powder, when potassa of soda is added to a solution of corrosive sublimate, or of nitrate of mercury. In this precipitated state it posesses certain properties in regard to solvents, which distinguish it from the crystalline oxide, of which it is considered an allotropic modification. Oxide of mercury has a metallic taste, and is poisonous; it is slightly soluble in water, and the solution, which is feebly alkaline, when exposed to air becomes gradually covered with a brilliant film. Its specific gravity is 11·074. When heated, it blackens, but becomes again red on cooling; at a red heat it evolves oxygen, and is reduced to the metallic state; it was thus that Priestley first obtained oxygen gas. When long exposed to light it becomes black upon the surface. It should be entirely volatilized when placed upon a red-hot iron, for it is sometimes adulterated with red lead. This oxide of mercury is decomposed by sulphur, phosphorus, and several of the metals: when mixed with sulphur and heated, it explodes; and with phosphorus it explodes by the blow of a hammer. It combines with acids, and like the suboxide forms compounds, several of which are resolvable into salts with excess of base, and salts with excess of acid. There is also a great tendency to the formation of double salts among the haloid mercurial compounds. The salts of the red oxide are, generally speaking, more active and poisonous than those of the black oxide; they mostly redden litmus, and are reduced first to the state of salts of suboxide, and then to metal, by several deoxidizimg agents, such as phosphorous and sulphurous acids, protochloride of tin and sugar.

Mercury and Chlorine combine in two proportions, and form a subchloride or dichloride, and a chloride or perchloride of mercury, compounds corresponding with the oxides, and formerly called *protochloride and bichloride;* the old terms *calomel* and *corrosive sublimate* applied to these chlorides are distinctively convenient.

Subchloride of Mercury; *Dichloride of Mercury.* Calomel (Hg_2,Cl). This compound is first mentioned by Crollius early in the seventeenth century. The first directions for its preparation are given by Beguin in 1608. There are several processes by which calomel may be obtained: one of these consists in triturating 4 parts of corrosive sublimate with 3 of mercury (and a little water to prevent the dust rising), till the whole forms a gray powder, which is introduced into a proper subliming vessel, gradually raised to a red heat: the subchloride sublimes, mixed with a little of the chloride, which may be separated by reducing the whole to fine powder, and washing it in large quantities of hot distilled water. In this process the chloride is reduced to the subchloride by the addition of mercury ($HgCl+Hg,=Hg_2,Cl$). Subchloride of mercury may also be formed by precipitating a solution of subnitrate of mercury by a solution of common salt: $Hg_2O,NO_5+NaCl=Hg_2Cl,+NaO,NO_5$. Calomel is generally manufactured upon the large scale, for pharmaceutical purposes, by sublimation, from a mixture of the sulphate of the suboxide with common salt: ($Hg_2O,SO_3,+NaCl,=Hg_2Cl+NaO,SO_3$). The calomel vapor is received into a capacious condenser, in which it is deposited in a pulverulent form: it is afterwards most carefully triturated, levigated, and washed in large quantities of distilled water, till it becomes perfectly tasteless, and till the water filtered from the washed powder is not discolored by sulphuretted hydrogen.

The form in which calomel sublimes depends much upon the dimensions and temperature of the vessel in which its vapor is condensed. In small vessels it generally condenses in a crystalline cake, the interior surface of which is often covered with prismatic crystals: in this state it acquires, by rubbing into powder, a pale buff tint. If, on the contrary, it is sublimed into a capacious and cold receiver, it falls in an impalpable white powder. By a modification of the process, it may be suffered, as it sublimes, to fall into water. But in whatever way calomel is obtained, it requires careful washing, and extreme care as to its state of minute mechanical division.

Calomel is tasteless, and insoluble in water. Its sp. gr. is 7·14. At a heat somewhat below redness, it rises in vapor, without previous fusion; but it fuses when heated under pressure. The density of its vapor is 8·2. By hot hydrochloric acid it is resolved into mercury and corrosive sublimate; but when boiled in dilute hydrochloric acid a portion is dissolved without decomposition. By nitric acid it is converted into corrosive sublimate and pernitrate, with the evolution of nitric oxide ($3Hg_2Cl+4NO_5=3HgCl+3[HgO,NO_5]+NO_2$). Sulphur, phosphorus, and several of the metals decompose it. Boiled with copper and water, chloride of copper and metallic mercury are procured. Triturated with iodine and water, corrosive sublimate and iodide of mercury are formed: $Hg_2Cl+I=HgCl+HgI$. With aqueous hydrocyanic acid calomel yields metallic mercury, and cyanide of mercury and hydrochloric acid are found in solution; $Hg_2Cl+HCy=Hg+HgCy+HCl$. *Native Subchloride of Mercury* or *Mercurial Horn Ore*, has been found crystallized, and sometimes incrusting and massive: it is rare.

CHLORIDE OF MERCURY.—*Perchloride. Bichloride. Oxymuriate of Mercury; Corrosive Sublimate* (HgCl).—When mercury is heated in excess of chlorine, it burns with a pale flame, and a white volatile substance rises, which is this chloride. When oxide of mercury is substituted for the metal, oxygen is expelled; $HgO+Cl=HgCl+O$: and when the oxide is gently heated in hydrochloric gas, water and the chloride are the results; $HgO+HCl=HgCl+HO$. The ordinary process for making corrosive sublimate consists in exposing a mixture of chloride of sodium and sulphate of mercury to heat in a proper subliming vessel; *corrosive sublimate* rises, and *sulphate of soda* is the residue; $HgO,SO_3+NaCl=NaO,SO_3+HgCl$.

Chloride of mercury has an acrid nauseous taste, leaving a permanent metallic and astringent flavor upon the tongue: it is a powerful corrosive poison. It evaporates to a small extent at common temperatures. Its specific gravity is 5·4. It is usually met with either in the form of heavy white semi-transparent and imperfectly crystallized masses, or in powder. It frequently exhibits prismatic crystals upon the inner surfaces of the sublimed cakes. It is soluble in about 16 parts of cold, and 3 of boiling water; and as the solution cools, it deposits quadrangular prismatic crystals. It dissolves in 3 parts of alcohol and in 4 of ether. When heated, it fuses, boils, and evaporates in the form of a dense white vapor, powerfully affecting the nose and mouth: the density of this vapor is 9·4: it is condensed in prismatic crystals on cold surfaces. Corrosive sublimate is nearly insoluble in concentrated nitric and sulphuric acids. Hydrochloric acid of the specific gravity 1·158, at the temperature of 60°, dissolves about its own weight, and the solution, when cooled to about 40°, concretes into a mass of crystals; there appear to be two or three of these *hydrochlorates of chloride of mercury;* they are partially decomposed when added to a great excess of water, and resolved into free hydrochloric acid and chloride.

Corrosive sublimate is either decomposed by, or combines with, many organic bodies; some of them convert it into calomel, others enter into combination with it, forming permanent compounds. The applications of it to the preservation of anatomical preparations, and to the prevention of dry rot, illustrate these actions. The efficacy of a mixture of white of egg and water, in preventing or mitigating the poisonous effects of this substance, depends upon its direct combination with albumen.

Oxichlorides of Mercury.—There are three of these compounds produced by the action of corrosive sublimate on bicarbonate of potassa; and each of them is said to be susceptible of allotropic modifications. If a saturated solution of the bicarbonate is added to 8 times its bulk of a saturated solution of the chloride, a red precipitate falls, which is $2(HgO)HgCl$; but with one volume of the alkaline solution, and two of the sublimate, the precipitate is black and crystalline, but of the same composition. When the solutions are mixed in equal volumes, the precipitate, which is at first yellow, is $3(HgO)HgCl$; and when the solution of sublimate is added to a large excess of that of the bicarbonate, carbonic acid is evolved, and brown crystalline crusts are deposited, which are $4(HgO)HgCl$.

ACTION OF AMMONIA ON CHLORIDE OF MERCURY.—When corrosive sublimate is heated in a stream of ammonia, a white crystalline, volatile, and fusible compound is obtained, which is not soluble in water without decomposition: it is *an ammonio-chloride*$=NH_3,2HgCl$. A solution containing 1 atom of sal-ammoniac and 1 of corrosive sublimate in a small quantity of water, yields rhombic prisms, permanent in the air, but which, when dried at 212°, become opaque, and lose about 5·5 per cent. of water. They constitute the *sal alembroth* of the old chemist$=NH_4Cl,HgCl$. When 1 atom of sal-ammoniac and 2 of corrosive sublimate are mixed and heated, a compound $=NH_4Cl+2HgCl$ sublimes: when the same salts are dissolved in water, the solution yields, on evaporation, silky crystals$=NH_4Cl+2HgCl+HO$.

AMIDOCHLORIDE OF MERCURY; *White Precipitate* ($HgNH_2,HgCl$) is obtained by adding a slight excess of ammonia to a solution of corrosive sublimate, washing the precipitate with cold water, and drying it by a gentle heat: $2HgCl+2NH_3=HgNH_2,HgCl+NH_4Cl$. It is a white powder, which, when boiled in water, is partly converted into sal-ammoniac which is dissolved, and partly into an almost insoluble yellow powder, which is a compound of amidide, chloride, and oxide of mercury: $2(HgNH_2HgCl)+2HO =NH_4Cl+(HgNH_2+HgCl+2HgO)$. When white precipitate is highly heated, a red crystalline compound remains, which is represented by the formula $2(HgCl)HgN$.

HYDRARGOCHLORIDES.—Chloride of mercury forms a numerous series of double salts with chlorides of the other metals, which are obtained by dissolving the salts in proper proportions, and allowing them to crystallize.

IODIDES OF MERCURY.—There are two iodides of mercury, corresponding to the chlorides.

SUBIODIDE (Hg_2I) is obtained, 1. By triturating together 200 parts of mercury and 126 parts of iodine, moistened with alcohol. 2. By adding iodide of potassium to a very dilute solution of acetate or nitrate of suboxide of mercury: $Hg_2O,NO_5+KI=Hg_2I+KO,NO_5$. 3. By digesting in boiling water 236 parts of calomel with 166 of iodide of potassium: $Hg_2Cl+KI= Hg_2I+KCl$. 4. By triturating together 1 equivalent of mercury with 1 of iodide of mercury, moistened with alcohol. Subiodide of mercury is a dingy greenish-yellow powder; specific gravity 7·7: it is nearly insoluble in water, and insoluble in alcohol. When rapidly heated in a glass tube it fuses, and sublimes unaltered: gently heated, or long exposed to light, it is resolved into mercury and iodide.

IODIDE.—*Periodide of Mercury* (HgI) is obtained, 1. By triturating 1 equivalent of mercury with 1 of iodine (100 mercury and 127 iodine) moistened with a little water or alcohol. 2. By the mutual decomposition of corrosive sublimate and iodide of potassium: $HgCl+KI=HgI+KCl$. When a strong solution of iodide of potassium is gradually added to one of corrosive sublimate, a red precipitate forms, which redissolves on agitation: forming a soluble compound of chloride and iodide of mercury; on the further addition of iodide of potassium a pale reddish and permanent precipitate is obtained, which is also a compound of chloride and iodide, containing, however, more of the latter; this precipitate, on continuing the addition of the iodide of potassium, becomes of a brilliant scarlet, and this is iodide of mercury, but if excess of iodide is added, it disappears, and a colorless solution of hydrargoiodide of potassium is formed; so that to obtain a pure iodide of mercury the relative atomic equivalents must be strictly preserved. When heated it becomes yellow, and fuses into an amber-colored fluid, giving off vapor which condenses in yellow rhombic plates: these, if scratched or ruptured, resume a scarlet color (p. 36).

Crystallizable double salts (*hydrargoïodides*) are formed by the combination of iodide of mercury with the alkaline iodides. The iodide is soluble in the chlorides of the metals of the alkalies, but does not form crystallizable compounds with them. When a hot solution of corrosive sublimate is saturated with iodide of mercury, it deposits crystals on cooling$=$HgI, 2HgCl.

SUBBROMIDE OF MERCURY (Hg_2Br) is obtained when 1 atom of mercury and 1 of bromide of mercury are mixed and heated; it forms a crystalline sublimate of a pale yellow color: it is also thrown down in the form of a white powder, on mixing solutions of bromide of potassium and nitrate of suboxide of mercury. It is insoluble in water, fusible, and volatile at a dull red heat.

BROMIDE OF MERCURY (HgBr) is formed by triturating mercury with bromine, or when bromine and mercury are shaken together in water. It is deposited from its aqueous solution in lamellar crystals, fusible and volatile. It is soluble in 100 parts of cold water, and in 4 or 5 of boiling water. It is very soluble in alcohol and in ether. An *oxybromide of mercury*$=$HgBr, 3HgO, is formed by boiling bromide and oxide of mercury together in water; it is a yellow crystalline powder, sparingly soluble in boiling water. There are several compounds of bromide of mercury with basic bromides (*hydrargobromides*), some of which are crystallizable.

MERCURY AND NITROGEN. NITRIDE OF MERCURY (Hg_3N).—This compound is formed by passing ammonia over oxide of mercury till saturated; it is then heated to 300°, and the current of ammonia continued as long as water is formed: $3HgO+NH_3=Hg_3N,+3HO$. The product is always contaminated by a little metallic mercury, which may be abstracted by cold dilute nitric acid. Nitride of mercury is a brown powder, which explodes when struck with a hammer, or when suddenly heated.

MERCURY AND NITRIC ACID. NITRATES OF MERCURY.—There appear to be three nitrates of the suboxide of mercury—namely, a neutral and two basic salts.

1. The *neutral Nitrate of suboxide of Mercury*$=Hg_2O,NO_5$, is formed by digesting excess of mercury in cold dilute nitric acid till *short prismatic crystals* are formed, which include 2 atoms of water. (If these are left in the solution they gradually give place to larger crystals of a sesqui-salt.) They are entirely soluble in a small quantity of warm water; by a large quantity of water they are resolved into an acid and basic salt: the *acid salt* is at once obtained by dissolving this, or the subnitrates, in dilute nitric acid. This salt is resolved by heat into red oxide (*Hydrargyri nitrico-oxidum*), and nitrous acid; ($Hg_2O,NO_5=2HgO+NO_4$). 2. *Sesquinitrate of suboxide of Mercury* ($3Hg_2O,2NO_5$).—When the first formed crystals of the preceding salt are left in the mother-liquor, they gradually dissolve, and are replaced by large transparent prisms having the formula $3Hg_2O,2NO_5,3HO$. They are soluble without decomposition in a little water; in much water they pass into a yellowish subsalt and a soluble supersalt.—3. *Bibasic nitrate of suboxide of Mercury* ($2(Hg_2O)NO_5$) is formed by repeatedly washing either of the preceding salts with cold water: it remains as a yellow crystalline powder.

Nitrates of the red oxide of Mercury; Pernitrates of Mercury.—1. There is no crystallizable *monobasic nitrate of red oxide of mercury*=HgO,NO_5. When peroxide of mercury is dissolved in nitric acid, or when mercury is boiled in strong nitric acid, a dense liquor is obtained on evaporation, which stains the cuticle brown; on further evaporation acid escapes and crystals of *dipernitrate* are formed. 2. *Bibasic nitrate of red oxide of Mercury. Dipernitrate of Mercury* $2(HgO)NO_5$. This salt, which crystallizes out of the preceding solution, is deliquescent, decomposed by water, but soluble without change in water acidulated by nitric acid: its crystals are $2(HgO)NO_5,2HO$. 3. *Tribasic nitrate of the red oxide of Mercury*=$3(HgO)NO_5,HO$, remains in the form of a yellow hydrated powder when the preceding salt is drenched with cold water as long as it runs off sour.—*Sexbasic nitrate of red oxide of Mercury*, $6(HgO)NO_5$, is formed by the continuous action of boiling water on the yellow tribasic salt.

Action of ammonia on the Nitrates of Mercury. 1. *Ammonio-nitrate of suboxide of Mercury. Hahnemann's Soluble Mercury* $(3Hg_2O,+NH_4O,NO_5)$. This compound is obtained by precipitating a very dilute cold aqueous solution of nitrate of suboxide of mercury by a weak solution of ammonia; the mixture should be constantly stirred, the ammonia not added in excess, and the precipitate washed as quickly as possible upon a filter, and dried in the shade at ordinary temperature. It is a grayish-black powder.—2. *Nitrate of ammonia and of suboxide of Mercury.* By evaporating a mixed solution of nitrate of suboxide of mercury and nitrate of ammonia, prismatic crystals are formed, the aqueous solution of which gives a gray precipitate both with ammonia and with carbonate of potassa.—3. *Basic amido-nitrate of Mercury* $(HgNH_2+5(HgO)NO_5)$. This compound appears to be sometimes formed when excess of ammonia is added to a concentrated nitrate of peroxide of mercury: it is a pale yellow powder containing about 85 per cent. of mercury.

MERCURY AND SULPHUR. *Subsulphide of Mercury; Disulphide of Mercury* (Hg_2S).—When 1 part of mercury is triturated for some time with 3 of sulphur, a black tasteless compound is obtained, which was called in old pharmacy *Ethiops mineral;* when boiled in solution of potassa, sulphur is taken up, and sulphide, (HgS) remains, so that it is probably a mixture of sulphur and sulphide. When sulphuretted hydrogen is passed through a dilute solution of nitrate of suboxide of mercury, or through a mixture of very finely divided calomel and water, a black powder is thrown down, which is a true subsulphide.

SULPHIDE OF MERCURY; *Bisulphide; Vermilion*; *Cinnabar* (HgS).—This sulphide is obtained anhydrous and of a red color by the following process: 6 parts of mercury are mixed in an iron pot with 1 of sulphur, and made to combine by a moderate heat, and constant stirring: the mixture is then transferred to a subliming-vessel, and heated to redness in a sand-bath. Mercury and sulphur evaporate, and a steel-gray sublimate forms, which is removed, and rubbed or levigated into a very fine powder (vermilion). If mercury and sulphur are heated together in large quantities, the action is so intense at the moment of their combination, as to occasion an explosive ignition. When solution of corrosive sublimate is decomposed by the prolonged action of an excess of sulphuretted hydrogen, or of an alkaline sulphide, the precipitate which falls is hydrated sulphide of mercury: it is black until warmed in the sulphuretted liquor, when it gradually reddens, as a result of dehydration. The principal points to attend to in procuring this pigment of its most perfect hue, are in the first place the careful selection and cleansing of the first crystalline gray sublimate, so that there may not be the smallest remaining admixture of the black pulverulent amorphous compound; and secondly, the perfection of the pulverization and elutriation, so as to render the powder as impalpable as possible. Cinnabar is not altered by exposure to air or moisture; when heated to a dull redness in an open vessel, the sulphur forms sulphurous acid, and the mercury escapes in vapor. The metal is thus procured from its ores (p. 446). In close vessels it sublimes before it fuses. It is decomposed by distillation with fixed alkalies, lime, and baryta, and by several of the metals. When adulterated with red lead or with colcothar, it is not entirely volatile. It is insoluble in caustic alkaline solutions, and in nitric and hydrochloric acids; but nitrohydrochloric acid acts upon, and decomposes it, even in the cold. Boiled in sulphuric acid, sulphurous acid is evolved, and a sulphate of mercury is formed. *Native Cinnabar* is the principal ore of mercury: it occurs massive and crystallized. It is of various colors, sometimes appearing steel-gray, at others bright-red. Native mercury, and native amalgam of silver, sometimes accompany it.

CHLOROSULPHIDE OF MERCURY ($2(HgS)HgCl$).—When sulphuretted hydrogen is passed through a solution of corrosive sublimate a white precipitate is first formed; if the action of the gas is continued, this white compound blackens and becomes hydrated sulphide of mercury. The same white compound is formed by digesting moist and recently precipitated sulphide of mercury, in a solution of corrosive sublimate. It may be washed and dried without decomposition. Corresponding compounds of the sulphide have been obtained with iodide and bromide of mercury. Sulphide of mercury also combines with other metallic sulphides.

SULPHATE OF SUBOXIDE OF MERCURY (Hg_2O,SO_3).—When 1 part of mercury is digested in a moderate heat with $1\frac{1}{2}$ of sulphuric acid, sulphurous acid gas is evolved, and a white mass is obtained, which, washed with cold water, affords a difficultly soluble white salt, which is a *sulphate of suboxide of mercury.* The same salt is thrown down, when sulphuric acid is added to a solution of nitrate of suboxide of mercury: it is also formed by triturating equivalent proportions of mercury and persulphate, and heating the mixture. In this way it is prepared for the manufacture of calomel. Sulphate of suboxide of mercury requires 500 parts of cold, and 300 of boiling water for its solution: it crystallizes in prisms.

SULPHATE OF PEROXIDE OF MERCURY; PERSULPHATE OF MERCURY (HgO, SO_3).—This salt is formed when two parts of mercury and three of sulphuric acid are boiled down to dryness. Sulphurous acid escapes in consequence of the decomposition of a portion of the acid ($Hg+2SO_3=HgO,SO_3+SO_2$). This sulphate is decomposed in the humid way by the hydracids, and free sulphuric acid is found in solution. It is resolved by water into a soluble acid salt and an insoluble basic salt: the former may be obtained in white deliquescent acicular crystals.—TRIBASIC SULPHATE OF PEROXIDE OF MERCURY; SUBSULPHATE OF MERCURY ($3(HgO)SO_3$). This salt, long known under the name of *Turpeth mineral* (so called from a similarity in its medicinal effects to those of the root of the *Convolvulus Terpethum,* which is cathartic and emetic), is obtained in the form of an almost insoluble yellow powder by the action of boiling water upon the preceding sulphate; when gently heated, its color gradually deepens to orange, but reverts to lemon-yellow as it cools.

Sulphate of Mercury forms a double salt with sulphate of ammonia = NH_4O,SO_3+HgO,SO_3, which is difficultly soluble, and falls in the form of a white powder on mixing solutions of the component sulphates.

PHOSPHATES OF MERCURY.—When solution of common phosphate of soda is dropped into a solution of suboxide of mercury, a white crystalline precipitate falls ($2(Hg_2O)HO,PO_5$); when the solution of the phosphate is added to pernitrate of mercury, a dense white insoluble powder is thrown down $=2(HgO)HO,PO_5$.

CARBONATES OF MERCURY.—*Carbonate of Suboxide of Mercury* (Hg_2O, CO_2) is thrown down when solution of carbonate of soda is dropped into solution of nitrate of suboxide of mercury, in the form of yellow powder. *Carbonate of Peroxide of Mercury* ($4(HgO)CO_2$).—Solution of nitrate of mercury affords a reddish-brown precipitate with carbonate of soda, which is slightly soluble in excess of the alkaline solution, and in aqueous carbonic acid.

MERCURY AND CYANOGEN. CYANIDE OF MERCURY ($HgCy$).—There are several processes for obtaining this compound. (1.) By boiling 1 part of finely-powdered peroxide of mercury with 2 of Prussian blue in 8 of water, a solution is obtained, which if filtered while hot, deposits crystals of the cyanide. (2.) When peroxide of mercury is brought into contact with the vapor of hydrocyanic acid they act intensely upon each other, and water and cyanide of mercury are formed. (3.) Peroxide of mercury may be digested in aqueous hydrocyanic acid. (4.) To a solution of 2 parts of ferrocyanide of potassium in 15 of boiling water, add 3 parts of dry persulphate of mercury; boil for 15 minutes and filter off the clear liquid whilst hot; as it cools cyanide of mercury crystallizes, which must be purified by a second crystallization; ($K_2FeCy_3+3HgO,SO_3=3HgCy+2KO,SO_3,+FeO,SO_3$). Cyanide of mercury forms anhydrous prismatic crystals, nearly colorless, or of a pale buff color, at first transparent, permanent in the air, poisonous, and of a nauseous metallic taste; they dissolve in 8 parts of water at 60°, and are sparingly soluble in alcohol. This salt is decomposed by heat, as in the process for obtaining cyanogen, and a brown or black matter remains in the retort, which is *paracyanogen* (p. 261). If distilled with hydrochloric acid, hydrocyanic acid and chloride of mercury are produced: it is also decomposed by hydriodic acid and by sulphuretted hydrogen, an iodide and a sulphide of mercury, and hydrocyanic acid, being formed (p. 266). Nitric acid dissolves it without decomposition. It is decomposed when heated with sulphuric acid. The alkalies do not act upon this cyanide.

FULMINATING MERCURY; FULMINATE OF MERCURY; ($2(Hg_2O)Cy_2O_2$).—This compound is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid, aided by heat. This solution is to be poured, when cool, into two measured ounces of alcohol in a porcelain basin, and gently warmed: it soon effervesces and evolves ethereal vapor, and if the action is too violent, it must be quelled by cooling the vessel, or by the addition of a little cold alcohol. During this action a gray precipitate falls, which is to be immediately separated by decantation and filtration, washed with small quantities of distilled water, and carefully dried at a heat not exceeding 100°. The above quantity of mercury should yield about 120 grains of the powder. If the product is mixed with metallic mercury, it may be purified by solution in boiling water, from which it is deposited in silky acicular crystals. This dangerous compound is now in considerable demand for the manufacture of percussion caps. It is introduced into the caps, closely compressed, moistened with a resinous varnish, and subsequently carefully dried. When fulminating mercury is heated to about 300°, it explodes suddenly with a bright flame: it also detonates by friction or percussion, especially when placed in contact with particles of sand or glass; by the electric spark, and by contact of concentrated sulphuric and nitric acids; the gases evolved by its explosions are carbonic acids, nitrogen, and the vapor of mercury.

ALLOYS OF MERCURY. *Amalgams.*—Mercury combines with most of the other metals, forming a class of compounds which are called *amalgams.* Many of these are definite and crystallizable, and may be separated, by gentle pressure, from the excess of mercury in which the definite compound is suspended or dissolved. They are generally brittle or soft. The extraordinary phenomena connected with the amalgam of *ammonium*, and the probable nature of that substance, have already been discussed (p. 169). One part of *potassium* with 70 of mercury produces a hard brittle compound. If mercury is added to the liquid alloy of *potassium and sodium*, an instant solidification ensues, and heat enough to inflame the latter metals is evolved. *Iron* and mercury may be combined by triturating together clean iron filings and zinc-amalgam, and adding a solution of perchloride of iron: by rubbing and heating this mixture, the iron and mercury form a bright amalgam. Under common circumstances, iron resists the action of mercury so perfectly, that the latter metal is usually kept in iron bottles; and mercurial troughs and barometer cisterns are made of iron. An amalgam of *zinc* is used for the excitation of electrical machines. 8 parts of mercury and 1 of zinc form a white brittle compound; 5 of mercury and 2 of zinc form a crystallizable amalgam. Amalgam of *tin* is easily formed by triturating the metals together, or by fusion at a gentle heat: it is largely used for silvering looking-glasses. This beautiful process is performed as follows: A single and perfect sheet of pure tinfoil, of proper thickness, and somewhat larger than the plate of glass, is spread upon a perfectly plane table of slate or stone: mercury is then poured upon it, and rubbed upon its surface by a hare's foot, or a ball of flannel or cotton, so as to form a clean and bright amalgam; upon this, an excess of mercury is poured, until the metal has a tendency to run off. The plate of glass, previously made quite clean, is now brought horizontally towards the table, and its edge so adjusted, as, by gradually and steadily sliding it forward, to displace some of the excess of mercury, and float the plate as it were over the amalgam, the dross upon its surface being pushed onwards by the edge of the glass, so that the mercury appears beneath it with a perfectly uniform, clean, and brilliant reflecting surface. Square iron weights, of 10 or 12 lbs. each, are then placed side by side upon the surface of the plate, so as entirely to cover it, and press it down upon the amalgamated surface of the tin; in this way the excess of mercury is partly squeezed out, and the amalgam is made to adhere, by crystallization, firmly to the glass (p. 23). The mercury, as it runs off, is received into a channel on the side of the table, which is slightly inclined to facilitate the drainage, and in about 48 hours the weights are taken off and the plate is carefully lifted from the table and set nearly upright, by which the adhering mercury gradually drains off, and the brilliant amalgam remains, perfectly and uniformly adhering to the glass. Amalgam of *copper* may be made as follows: to a hot solution of sulphate of copper add a little hydrochloric acid and a few sticks of zinc, and boil the mixture for about a minute; the copper will be precipitated in a metallic state, and in a finely-divided spongy form; take out the zinc, pour off the liquor, wash the copper with hot water, and pour upon it a little dilute nitrate of mercury, which will instantly cover every particle of copper with a coating of this metal; then add mercury to the amount of two or three times the weight of the copper, and a slight trituration will so combine them that the completion of the process may be effected by heating the mixture for a few minutes in a crucible. *Lead* and mercury readily combine in all proportions: 3 parts of mercury and 2 of lead form a crystallizable amalgam. *Bismuth* and mercury readily unite: a mixture of 3 parts of mercury, 1 of lead, and 1 of bismuth forms a fluid amalgam used for silvering the inside of hollow glass spheres. When mercury is adulterated, it is with these metals; but the facility with which it then oxidizes, and the imperfect fluidity of its small globules, render the fraud easy of detection.

TESTS FOR THE SALTS OF MERCURY.—The soluble salts of the *suboxide* are mostly white: some of them, when neutral, are resolved by water into basic and acid salts. 1. With phosphorous and sulphurous acids, and protochloride of tin, they give precipitates of metallic mercury; 2. The caustic alkalies throw down a black, and the carbonated alkalies a yellow or brown precipitate; 3. The alkaline phosphates, a white precipitate, even in very dilute solutions; 4. Sulphuretted hydrogen and the hydrosulphates, black; 5. Hydriodic acid and the iodides, dingy green or yellow in very diluted solutions; 6. Hydrochloric acid and the chlorides, white and curdy precipitates; the alkaline chromates, red; ferrocyanide of potassium, white; the oxalates, white, even when very dilute. The soluble salts of the red or *peroxide* of mercury are mostly white when neutral, yellow when basic, and are often resolved by water into acid and basic salts. 1. Protochloride of tin gives a black precipitate, which, when boiled, thrown on a filter, and dried, runs into small globules of metallic mercury. 2. Caustic alkalies, when added in small quantity, give a reddish-brown, and in large quantity, a yellow precipitate of the hydrated oxide of mercury. 3. Ammonia and carbonate of ammonia produce white precipitates in their solutions. 4. Iodide of potassium gives a red, and infusion of galls an orange precipitate. Unless in concentrated solutions they are not affected by hydrochloric or oxalic acid. Metallic mercury is precipitated from all of its solutions by a plate of clean copper. The insoluble mercurial salts are mostly volatilized at a red heat; and both soluble and insoluble salts are decomposed, with the production of metallic mercury, when heated in a glass tube with 2 or 3 parts of dry carbonate of soda, or of ferrocyanide of potassium.

ANALYSIS IN CASES OF POISONING.—*Oxide of Mercury* may be identified by its red color, its insolubility in water, and by its yielding a sublimate (in globules) of metallic mercury, when dried and heated in a glass tube. It is dissolved by nitric acid, and the solution possesses the characters assigned above to the persalts of the metal. *White precipitate.* This is a white chalky-looking powder, not soluble in water, but partly converted into a yellow basic salt by boiling water: 1. Ammonia does not change its color. 2. Nitric acid readily dissolves it (by these two characters it is distinguished from calomel); in the acid solution, chlorine may be found by the addition of nitrate of silver. 3. When boiled with a solution of potassa, ammonia is liberated. 4. When digested with protochloride of tin, it is darkened, and metallic mercury is set free. 5. When heated with dry carbonate of soda, it yields a sublimate of metallic mercury.

Corrosive Sublimate.—This is the principal poison of mercury. It is usually seen in heavy crystals, or in the form of a white crystalline powder. As a *solid*, 1. When the powder is heated on a platinum foil or mica, it melts, and is volatilized in a white vapor without leaving any residue. 2. When heated in a close tube, it melts and forms a sublimate, consisting of prismatic crystals sometimes stellated. 3. The powder is changed in color by the following reagents: iodide of potassium produces a bright scarlet, potassa a yellow, and hydrosulphate of ammonia a black precipitate; ammonia does not alter it. 4. The mercury and chlorine may be discovered by one process. Mix the powder with 3 parts of dry carbonate of soda, and heat it until the residue in the tube fuses and becomes white. A sublimate of metallic mercury in globules will be obtained. Detach by a file the end of the tube containing the fused residue, which is chloride of sodium with some undecomposed carbonate. Digest it in water with nitric acid, and apply heat until it is entirely dissolved: then add to the solution, nitrate of silver. A white precipitate of *chloride* of silver, insoluble in nitric acid will be at once produced. The solid is thus proved to contain both mercury and chlorine, and the only compound of these elements soluble in water is corrosive sublimate. In *solution* in water. 1. Protochloride of tin added to a solution of corrosive sublimate, produces a black precipitate which, after it has been boiled, is resolved into globules of metallic mercury. 2. Sulphuretted hydrogen and hydrosulphate of ammonia produce, after a time, a black sulphide, not soluble in alkalies or diluted acids. 3. If the liquid is acidulated, and bright copper foil, wire, or gauze, is plunged into it, the copper acquires a silvery-white deposit, even in the cold, but more rapidly by heat. When the copper with the metallic deposit is heated in a tube, globules of mercury are obtained.

In Organic Liquids.—The liquid should be separated by filtration from any insoluble portion. The latter should be pressed, dried, and set aside for a separate analysis. A slip of bright copper foil or gauze may be employed as a trial test in the manner above described. In place of copper, a small galvanic combination, made by twisting a layer of gold-foil round a layer of zinc foil, may be introduced. The liquid should be slightly acidulated with hydrochloric acid and warmed. The metals may be suspended in the liquid for some hours. If the mercurial poison is present, the gold will sooner or later lose its color and become silvered while the zinc will be wholly or in part dissolved. The slip of gold foil may be washed in water, and afterwards in ether, and dried. It should be divided into two equal portions. One should be submitted to heat in a tube, when globules of mercury will be obtained; the other should be heated in concentrated nitric acid, until the gold has reacquired its yellow color. On evaporating the excess of acid, and adding a solution of protochloride of tin, a dark gray precipitate of metallic mercury is thrown down. It may be remarked that sublimed mercury is wholly unlike any other volatile substance. Globules of the 8000th part of an inch in diameter may be easily recognized by the aid of a microscope. Their perfect sphericity, their silvery whiteness by reflected, and complete opacity by transmitted light, at once identify them as metallic mercury.

In the event of a doubt existing respecting their mercurial nature, the following experiment will remove it. Cut off by a file the portion of glass in which they are deposited: introduce this into a wide short tube, with a few drops of hydrochloric, and half the quantity of nitric acid. Heat the acid liquid, and carry it to dryness on a sand-bath. White prismatic crystals of corrosive sublimate will remain if the sublimate was of a mercurial nature, and too great a heat has not been applied. On touching the white residue cautiously with a drop of solution of iodide of potassium, the crystals will acquire a scarlet-red color.

Another method of analysis may be sometimes usefully resorted to. Place the suspected organic liquid in a small golden capsule. Acidulate it slightly with hydrochloric acid, and touch the gold, through the acid liquid, with a slip of pure zinc foil. Mercury will be deposited in a white silvery stain on the gold, wherever the two metals have come into contact. Wash out the capsule with distilled water, and add a few drops of strong nitric acid. Pernitrate of mercury is thus obtained, which may be tested by the processes above described for the detection of the persalts of mercury.

The insoluble compounds of mercury may be dissolved by strong nitric acid, and the solution tested for the metal. If none is found, the dried solid, mixed with dried carbonate of soda or ferrocyanide of potassium, may be heated in a tube, when mercury, if present, will be volatilized. The *tissues* may be dried and dissolved in 1 part of hydrochloric acid and 4 parts of water. The metal may be separated from the concentrated liquid, either by copper-gauze or by gold and zinc.

The processes above described reveal only the presence of mercury. When the quantity of corrosive sublimate in an organic liquid is moderately large, it may be removed by means of ether. Place the filtered liquid supposed to contain the poison, in a stoppered tube; add to it, its volume of pure ether, and agitate the liquid at intervals for half an hour. Allow the liquid to subside, pour off the ether into a dial-glass, and submit it to spontaneous evaporation. As the ether passes off, the corrosive sublimate will be deposited in white silky-looking prisms. These may be purified by solution in water, if necessary, and the solution again crystallized. If mercury and arsenic are associated in a poisonous mixture, the arsenic may be entirely separated by distillation (page 446).

CHAPTER XXXVIII.

SILVER ($Ag=108$).

THIS metal, the *Luna* or *Diana* of the alchemists (☽), was known at a very remote period: it is found *native*, and in a variety of combinations, the most common of which is the *sulphide*. *Native Silver* occurs massive; arborescent; capillary; and, sometimes, crystallized. It is seldom pure, but contains other metals, which affect its color and ductility.

Silver is not unfrequently obtained in considerable quantities from *argentiferous sulphide of lead*, which is reduced in the usual way, and the argentiferous lead is then fused in a shallow dish, placed in a reverberatory furnace, with a current of air constantly passing over its surface; in this way the lead is converted into oxide or *litharge*, and the silver is left in the metallic state. The litharge which results from this operation is afterwards reduced by charcoal, and furnishes lead which is free from silver; the ordinary lead of commerce generally contains a trace of the latter metal, and is consequently unfit for certain purposes of the arts, especially for the manufacture of white lead.

The sulphides of silver are reduced by *amalgamation*. The ore, when washed and ground, is mixed with a portion of common salt, and roasted: during this operation arsenic and antimony are expelled, the copper and the iron are converted into oxides, chlorides, and sulphates, and sulphate of soda and chloride of silver are formed. The product is powdered, and agitated with mercury, water, and filings or fragments of iron; in this operation the chloride of silver is decomposed, chloride of iron is formed which is washed away, and the silver and mercury combine into an amalgam, from which the excess of mercury is first squeezed out in leather bags, and the remainder driven off by distillation. The old process of *eliquation* is now scarcely used: it consisted in fusing alloys of copper and silver with lead; this triple alloy was cast into plates which were placed in a proper furnace upon an inclined plane of iron with a small channel grooved out, and heated red-hot, during which the lead melted, and in consequence of its attraction for silver, carried that metal with it, the copper being left behind in a reddish-black spongy mass. The separation of silver from lead by the process of crystallization has been already noticed (page 26).

Pure Silver may be procured by dissolving the standard silver of commerce in nitric acid, diluted with an equal measure of water. Immerse a plate of clean copper in the filtered solution, which occasions a precipitate of metallic silver; collect it upon a filter; wash it with a weak solution of ammonia, and then with water, and fuse it into a button. It may also be procured by adding to the above solution of standard silver a solution of common salt; collect, wash, and dry the precipitate, and gradually add it to twice its weight of fused carbonate of potassa mixed with carbonate of soda, in a red-hot crucible. Metallic silver is separated, and may be fused into a button.

Properties.—Silver is of a more pure white than any other metal: it has considerable brilliancy, and takes a high polish. Its specific gravity varies between 10·4, which is the density of cast silver, and 10·5 to 10·6, which is the density of rolled or stamped silver. It is so malleable and ductile that it may be extended into leaves not exceeding a ten-thousandth of an inch in thickness, and drawn into wire infinitely finer than a human hair. Silver melts at a bright red heat, estimated at 1873° of Fahrenheit's scale, and when in fusion appears extremely brilliant. It resists the action of air at high temperatures for a long time, and does not oxidize; the *tarnish* of silver is occasioned by sulphuretted hydrogen; it takes place very slowly upon the pure metal, but more rapidly upon the alloy with copper used for plate. Pure water has no effect upon the metal; but, if the water contains organic matter, it is sometimes slightly blackened. If an electric discharge is passed through fine silver-wire, it burns into a black powder. In the Voltaic circle it burns with a fine green light, and throws off abundant fumes. Exposed to an intense white-heat in the open fire it boils and evaporates, but in close vessels it is not sensibly volatile. If suddenly cooled, it crystallizes during congelation, often shooting out like a cauliflower, and *spirting* or throwing small particles of the metal out of the crucible. This arises from the escape of oxygen, which the metal absorbs and retains whilst fluid, but suddenly gives off when it solidifies: this curious property of absorbing oxygen is prevented by the presence of a small quantity of copper.

OXIDES OF SILVER.—There are three oxides of this metal—a suboxide, Ag_2O; a protoxide, AgO; and a binoxide, AgO_2. Of these, the protoxide only forms permanent and definite saline combinations. 1. *Suboxide of Silver* (Ag_2O). This oxide is obtained by the action of hydrogen on citrate of silver, at the temperature of 212°; the protoxide loses half its oxygen, and the suboxide remains combined with half of the acid. The solution in water of the suboxide salt is dark-brown, and the suboxide is precipitated black from it by potassa; when the solution of the subsalt is heated, it becomes colorless, and metallic silver appears in it. Some other salts of silver, containing organic acids, may be substituted for the citrate. 2. *Oxide of Silver* (AgO) may be obtained by adding a dilute solution of potassa to a solution of nitrate of silver, washing the precipitate, and drying it at 212°. It is of a dark olive color, tasteless, but soluble to a small extent in pure water; and, like oxide of lead, it has when in solution an alkaline reaction: this solution is reddened by exposure to light, and is rendered turbid by a little carbonic acid, but again becomes clear with an excess. When heated to dull redness this oxide is reduced to the metallic state; long exposure to light also reduces it, converting it into a black powder, which is either silver or its suboxide. It is reducible by hydrogen at a temperature of about 212°; and also by phosphorous and sulphurous acids. It imparts by fusion a yellow color to glass, and is employed in enamel and porcelain painting. Oxide of silver dissolves in aqueous ammonia, forming a colorless liquor, which becomes coated with a film of suboxide by exposure to air; and when kept for some months in a stopped bottle, acquires a film of metallic silver. Berthollet's fulminating silver is also formed by the action of ammonia on the oxide. The best process for preparing it is to pour a small quantity of strong aqueous ammonia upon the oxide; a portion is dissolved, and a black powder remains, which is the detonating compound: it should be cautiously dried on bibulous paper. It explodes with tremendous violence when gently rubbed or heated; nitrogen and water are evolved, and the silver is reduced. It should only be prepared in small quantities, and handled with caution, for it occasionally explodes while wet. It is soluble in ammonia, and this solution sometimes deposits it in small brilliant opaque crystals. There is some doubt respecting the real nature of this compound: it is probably a nitride of silver, $=Ag_3N$. The composition usually assigned is $3(AgO)NH_3$; when exploded, it is converted into $3Ag+N+3HO$.

Peroxide of Silver (AgO_2).—By electrolyzing a weak solution of silver, acicular crystals of this peroxide are formed at the positive pole. Ammonia energetically decomposes it, and acids convert it into the protoxide. When mixed with phosphorus or sulphur, and struck with a hammer, it detonates.

Chloride of Silver ($AgCl$).—When silver leaf is acted upon by gaseous chlorine in a humid state, it is gradually converted into this compound, and if sufficiently thin, a leaf of white chloride of silver is obtained in a few hours; otherwise the action is superficial. Chloride of silver is usually procured by adding a solution of common salt to a solution of nitrate of silver. It falls in the form of a white curdy precipitate, which, by exposure to light, becomes violet-colored, brown, and ultimately black. This happens even in diffused daylight, but in sunshine the change is rapid, especially if organic matter or moisture is present. This property of the chloride has led to its employment in photography. (*See* p. 468.) When a small quantity of subchloride of mercury is precipitated along with the chloride of silver, the blackening effect of light is greatly diminished. Chloride of silver is so insoluble in water, that the minutest portion of hydrochloric acid, or of any chloride in aqueous solution, may be detected by it. It is insoluble in nitric acid, and in cold sulphuric acid; but when boiled in sulphuric acid, it is slowly decomposed, with the formation of sulphate of silver. It is soluble to a small extent in boiling hydrochloric acid, and in strong solutions of the chlorides of the alkaline metals, forming with them crystallizable double salts. It is abundantly soluble in solutions of ammonia, cyanide of potassium, and the alkaline hyposulphites.

When dry chloride of silver is heated to dull redness in a silver crucible, it does not lose weight, but fuses, and, on cooling, concretes into a gray semitransparent substance (sp. gr. 5·45), which has been called *horn silver*, or *luna cornea*. If slowly cooled, it has a tendency to octahedral crystallization. Heated to a bright red or white heat in an open vessel, it volatilizes in dense white fumes. If fused with potassa or soda, or their carbonates, chloride of silver is decomposed, and metallic silver is obtained; ($AgCl+KO=Ag+KCl+O$). Moist chloride of silver is also decomposed when triturated with, and boiled in a solution of caustic potassa; a dense black oxide is produced, and if sugar is added, it is reduced to metallic silver. It is also decomposed, when moist, by zinc, iron, and some other metals, especially if aided by heat and by a little hydrochloric acid. In the latter case hydrogen is liberated, and the silver is completely reduced ($AgCl+H=Ag+HCl$). Triturated with fine zinc filings, and moistened, the heat produced is considerable. The fused chloride, exposed to ammonia, absorbs a considerable portion of the gas, which is again given off by heat. If the chloride, thus saturated with ammonia, is thrown into chlorine, the ammonia spontaneously inflames.

As chloride of silver is insoluble in water, a salt of silver is employed in quantitative analysis, as a means of ascertaining the proportion of chlorine. In these cases some excess of the precipitant should be used, and the precipitate allowed to subside previous to separating it upon the filter: if the supernatant liquor becomes perfectly clear, the whole of the silver has fallen; if it remains opalescent, a portion is probably still retained. When the precipitate remains long suspended, its deposition may be accelerated by heat, by agitation, or by adding a little nitric acid. The chloride should be perfectly dried before weighing it. 100 parts of the dried and fused chloride, are equivalent to 24·67 parts of chlorine and 75·33 of silver.

Native Chloride of Silver has been found in most of the silver-mines; it occurs massive and crystallized.

IODIDE OF SILVER (AgI).—When silver-leaf is put into a bottle containing a little iodine it is speedily tarnished, and in the course of a few days converted into a film of yellow iodide. Iodide of silver is precipitated upon adding a soluble iodide to a solution of nitrate of silver. It is of a yellowish color, insoluble in water, and decomposed when heated with potassa. Chlorine also decomposes it. It is nearly insoluble in ammonia. When fused, it acquires a red color. It dissolves in solutions of the alkaline cyanides and hyposulphites, and in a saturated solution of nitrate of silver: it is also dissolved by iodide of potassium and other alkaline iodides. *Native Iodide of Silver* has been found in some of the Mexican ores, associated with native silver, sulphide of lead, and carbonate of lime.

BROMIDE OF SILVER ($AgBr$) is an insoluble yellowish substance, thrown down upon the addition of bromine, or the soluble bromides, to nitrate of silver: it dissolves in an excess of a strong aqueous solution of ammonia, and readily in alkaline cyanides and hyposulphites: it is fusible, and concretes on cooling into a yellow corneous mass. Chlorine converts it into chloride of silver: it is sparingly soluble in solutions of bromide of potassium and sodium, and more abundantly so in a solution of sal-ammoniac: the compounds which it forms with the alkaline bromides are decomposed when diluted. *Native bromide of silver* has been found in Mexico and Chili, in small yellowish cubic crystals; and a native *chlorobromide* ($3AgCl,2AgBr$) from Chili has been described by Colonel Yorke.

NITRATE OF SILVER (AgO,NO_5).—Nitric acid diluted with 3 parts of water readily dissolves silver, with the disengagement of nitric oxide: if the silver contains copper, the solution is bluish; or if gold, that metal remains undissolved in the form of a black powder. The solution of nitrate of silver should be clear and colorless; it is caustic, and tinges animal substances at first of a yellow color, becoming, by exposure to light, purple or black. On evaporation, the solution yields anhydrous tabular crystals, which have a bitter metallic taste, and are soluble in about their own weight of water at 60°, and in half their weight at 212°: they are insoluble in nitric acid. Alcohol dissolves about one-fourth its weight of this salt at its boiling-point, but deposits nearly the whole as it cools. Nitrate of silver, when mixed with organic matters, blackens on exposure to light; and when thus acted upon, it is no longer perfectly soluble in water, owing to the separation of a portion of metallic silver; but if cautiously excluded from the contact of organic matter, light alone does not discolor it. When heated in a silver crucible, it fuses into a gray mass, and if cast into small cylinders, forms the *lunar caustic* of pharmacy. When nitrate of silver is exposed to a red heat, the acid is partly evolved and partly decomposed, and metallic silver is obtained. Sulphur, phosphorus, charcoal, hydrogen, and several of the metals, decompose this nitrate. A few grains mixed with a little sulphur, and struck upon an anvil with a heavy hammer, produce a detonation: phosphorus occasions a violent explosion when about half a grain of it is placed upon a crystal of the nitrate and struck sharply with a hammer; if heated with charcoal it deflagrates, and the metal is reduced.

A stick of phosphorus or charcoal introduced into a weak solution of nitrate of silver, soon becomes incrusted with crystals of silver. A plate of copper also occasions a precipitation of crystalline silver. Mercury introduced into a solution of nitrate of silver causes a crystalline deposit of silver, called the *arbor Dianæ*. Protosulphate of iron throws down metallic silver when added to a solution of the nitrate; protochloride of tin forms a gray precipitate.

When some of the solutions of silver are reduced by certain essential oils, or by grape-sugar, a brilliant film of the metal may be so thrown down upon glass as to furnish a substitute for the amalgam of tin usually employed for mirrors: the coating is not to be depended upon for durability, but it has the advantage of being applicable to curved surfaces and the interior of spherical vessels. Pelouze and Frémy describe the process as follows: 600 grains of nitrate of silver are dissolved in 1200 grains of water; to this are added, 1st. 75 grains of a solution composed of 10 grains of sesquicarbonate of ammonia, 10 of solution of ammonia, sp. gr. 0·980, and 25 of distilled water; 2d. 30 grains of solution of ammonia, sp. gr. 0·980; 3d. 1000 grains of alcohol, sp. gr. 0·850: this mixture is left at rest to become clear, it is then decanted, and a mixture of equal parts of alcohol and of oil of cassia is added, in the proportion of 1 part of this *essence of cassia* to 15 parts of the solution of silver: this mixture is shaken and left to settle for some hours, and then filtered: just before applying it to the glass to be silvered, it is mixed with 1-78th of its bulk of *essence of cloves*, composed of 1 part of oil of cloves and 3 of alcohol. The glass to be silvered is first thoroughly cleansed, then covered with the silvering solution and warmed to about 100°, at which temperature it is kept for two or three hours: the liquid is then decanted and may be used for other glasses. The deposit of silver is then washed, dried, and varnished.

Nitrate of silver is employed for writing upon linen, under the name of *indelible* or *marking ink:* and it is an ingredient, with gallic acid, in some of the liquids sold for the purpose of changing the color of hair: the black stain of any of these preparations of silver may be removed by cyanide of potassium. When taken internally, a discoloration of the *rete mucosum* often ensues, so that the whole surface of the body, and especially the parts exposed to light, acquire a leaden-gray color.

Solution of the nitrate of silver is a valuable test of the presence of chlorine, hydrochloric acid, and the soluble chlorides, with which it forms a white cloud when very dilute, but a flaky precipitate when more concentrated; the precipitate is soluble in ammonia, but insoluble in nitric acid. Heat, agitation, or the addition of a few drops of nitric acid, so as to render the liquid acid, facilitates the deposition of the precipitate. The hydriodic, hydrobromic, and hydrocyanic acids also occasion in a solution of nitrate of silver, precipitates which become slightly darkened by exposure to light.

AMMONIO-NITRATE OF SILVER.—Ammonia is rapidly absorbed by nitrate of silver, with the production of heat sufficient to fuse the compound, which consists of 100 parts of the nitrate, and 29·5 parts of ammonia. An ammonio-nitrate of silver is also obtained when ammonia is added to a solution of nitrate of silver until the first-formed precipitate is redissolved. This solution when colored with a little Indian ink forms a good marking ink, but the stains of all these compounds may be removed by cyanide of potassium: or by steeping the linen in chlorine water until the stain is whitened, and then applying ammonia or a solution of hyposulphite of soda to dissolve and wash out the chloride.

SULPHIDE OF SILVER (AgS).—Silver readily combines with sulphur, and produces a gray crystallizable compound, more fusible and softer than silver. It may be obtained by heating finely-divided silver, or plates of silver, with sulphur. Its density is about 7. Sulphuretted hydrogen and hydrosulphate of ammonia occasion a copious black precipitate of sulphide of silver when added to solutions of the metal: sometimes a portion of the silver is at the same time reduced to the metallic state. It is the presence of sulphur in the atmosphere (generally sulphuretted hydrogen) which occasions the tarnish upon silver, and which is a great obstacle to many applications that might otherwise be made of this beautiful metal.

Native Sulphide of Silver, or *vitreous silver*, is found massive and crystallized. It is soft and sectile. A triple combination of *silver*, *antimony*, and *sulphur*, $=3(AgS)SbS_3$, constitutes the *red* or *ruby silver-ore;* it is sometimes accompanied by the *brittle sulphide*, or *silver glance*, and by *antimonial silver* (Ag_2Sb).

HYPOSULPHITE OF SILVER ($AgO,S_2O_2,5HO$) is formed by dropping a weak solution of nitrate of silver into a solution of hyposulphite of soda: a white cloud is produced, which redissolves on agitation; on adding more of the precipitant, the cloud reappears and aggregates into a gray precipitate of hyposulphite of silver. When the nitrate is in excess, the precipitate rapidly changes from gray to yellow, brown, and black, being ultimately converted into sulphide of silver. Hyposulphite of silver is also produced when chloride of silver is dissolved in any of the hyposulphites; the solution has a sweetish taste. This solubility of argentine compounds in alkaline hyposulphites, has led to the important application of them to the photographic art. (*See* PHOTOGRAPHY, p. 476.) Hyposulphite of silver is very prone to decomposition, especially on boiling, being resolved into sulphate of oxide of silver, and sulphide of silver.

Double salts of the hyposulphites of ammonia, potassa, and soda, with silver, have been formed.

SULPHITE OF SILVER (AgO,SO_2) is obtained in white crystalline grains by adding an alkaline sulphite to a solution of silver. It produces double salts with the sulphites of the alkalies.

SULPHATE OF SILVER (AgO,SO_3) is deposited when sulphate of soda is mixed with nitrate of silver. It is also produced by boiling silver with its weight of sulphuric acid. It forms a white salt soluble in about 90 parts of water at 60°; in boiling water it is more soluble, and is deposited, as the solution cools, in small anhydrous crystals: it dissolves in sulphuric acid, but on moderate dilution, the greater part of the salt again falls down. By leaving a strong sulphuric solution of silver in a dark place, it gradually absorbs water, and octahedral crystals of the sulphate are deposited. Upon the large scale, small portions of gold are separated from large quantities of silver, by heating the finely granulated alloy in sulphuric acid: the gold remains in the form of a black powder, and the sulphate of silver may be decomposed by the action of metallic copper, which precipitates metallic silver, and forms sulphate of copper. Sulphate of silver absorbs ammonia, and by saturating a strong and warm solution of ammonia with sulphate of silver, prismatic crystals$=2(NH_3),AgO,SO_3$, are obtained.

PHOSPHATE OF SILVER $3(AgO)PO_5$.—When a solution of common phosphate of soda, $2(NaO)HO,PO_5$, is added to nitrate of silver, a yellow anhydrous tribasic phosphate of silver falls, and free nitric acid is found in the supernatant liquor: $3(AgO,NO_5)+2(NaO)HO,PO_5=3AgOPO_5+2(NaO,NO_5)+HO,NO_5)$. If the solution of nitrate of silver is precipitated by anhydrous tribasic phosphate of soda, $3(NaO)PO_5$, the supernatant solution remains neutral. This phosphate of silver fuses at a red heat. It is soluble in nitric, phosphoric, and acetic acids, as well as in ammonia and carbonate of ammonia.

PYROPHOSPHATE OF SILVER, $2(AgO)PO_5$, is the *white* precipitate thrown down from nitrate of silver by pyrophosphate of soda: in this case the supernatant liquid remains neutral [$2(AgO,NO_5)+2(NaO)PO_5=2(AgO)PO_5+2(NaO,NO_5$].

METAPHOSPHATE OF SILVER (AgO,PO_5) is a white gelatinous precipitate, thrown down by a solution of nitrate of silver by metaphosphate of soda; boiling water resolves it into an acid and a basic salt.

CARBONATE OF SILVER (AgO,CO_2) is precipitated in the form of a pale yellow powder, by adding carbonate of potassa to nitrate of silver. It blackens by exposure to light, and is easily decomposed by heat. Moist oxide of silver absorbs carbonic acid from the air.

CYANIDE OF SILVER ($AgCy$).—Hydrocyanic acid, or solution of cyanide of potassium, causes a white precipitate in solution of nitrate of silver, which is *cyanide of silver*, and which, when heated, fuses, and, at a high temperature, gives out cyanogen. It is insoluble in water and in fixed alkalies, but soluble in ammonia. It is decomposed by hydrochloric acid, and by sulphuretted hydrogen; nitric acid scarcely acts upon it, unless concentrated and heated. Sulphuric acid, diluted with its volume of water, decomposes it when boiling, with the escape of hydrocyanic acid and the formation of sulphate of silver: in this way cyanide may be separated from chloride of silver. It dissolves in a strong solution of nitrate of silver, and forms a compound which is decomposed by water. It is soluble in the alkaline chlorides, in hyposulphite of soda, and in cyanide of potassium. *Argento-cyanides.* Cyanides of the alkaline bases form soluble double salts with cyanide of silver: they are insoluble in alcohol, which throws them down from their aqueous solutions. The *argento-cyanide of potassium* ($KCy,AgCy$) yields plumose colorless crystals: it produces precipitates in many of the metallic solutions, which are *insoluble argento-cyanides.* A solution of oxide or chloride of silver in cyanide of potassium, forms a useful liquid for silvering metals by immersion, especially when aided by electricity. It is thus employed in *electro-plating:* 1 part of cyanide of potassium may be dissolved in 10 parts of water, and 50 or 60 grains of oxide or chloride of silver dissolved in each pint: the oxide and chloride should be in a moist state.

CYANATE OF SILVER (AgO,CyO).—This monobasic salt falls in the form of a white powder when cyanate of potassa is added to nitrate of silver.

FULMINATE OF SILVER; FULMINATING SILVER, $2(AgO)Cy_2O_2$.—This dangerous compound is prepared as follows: 100 grains of fused and finely-powdered nitrate of silver are added to an ounce of warm alcohol in a large basin; an ounce of nitric acid is then added, and presently effervescence ensues and a powder falls: as soon as this appears white, cold water is added, and the powder collected upon a filter, washed, and carefully dried at a temperature of 100°. In collecting and handling this powder the utmost caution is requisite; it should be made in small quantities only, and not touched with anything hard, for it has exploded upon the contact of a glass rod under water. The feather of a common quill serves to collect it; and it should be kept either under water, or if dry, in a wide-mouthed vessel covered by paper, and *not* in a stoppered or corked phial. Fulminating silver is a gray crystalline powder; it acquires a dingy hue by exposure to light; it dissolves in from 30 to 40 parts of boiling water, and as the solution cools, nearly the whole is again deposited in minute crystals. It detonates with great violence when heated, or when touched by any hard substance; placed upon a piece of rock-crystal and touched in the slightest manner by another crystal, it explodes violently; it also detonates upon the contact of sulphuric acid, and by the electric spark. In the formation of fulminic acid, a portion of the alcohol is oxidized so as to form aldehyde, and formic and oxalic acids: this is effected at the expense of the oxygen of the nitric acid, which passes into hyponitrous acid, and this, reacting upon another portion of the alcohol, forms hyponitrous ether, fulminic acid, and water; 1 atom of hyponitrous ether and 1 of hyponitrous acid containing the elements of 1 atom of fulminic acid and 5 of water.

$$\underbrace{\text{Hyponitrous Ether}}_{C_4H_5O,NO_3} + \underbrace{\text{Hyponitrous Acid}}_{NO_3} = \underbrace{\text{Fulminic Acid}}_{C_4N_2O_2} + \underbrace{\text{Water}}_{5HO}$$

When fulminating silver ($2(AgO)Cy_2O_2$) is digested in a solution of potassa, half the oxide of silver is precipitated, and on filtering and evaporating the solution, a crystallizable salt is obtained$=AgO,KO,Cy_2O_2$. It is dangerously explosive. In this salt one atom of oxide of silver is replaced by one atom of potassa. Corresponding compounds may be obtained with other basic oxides.

CYANURATE OF SILVER.—If nitrate of silver is added to cyanurate of potassa, a white precipitate is obtained, which consists of 1 atom of cyanuric acid combined with 2 of oxide of silver and 1 of water: $2(AgO)HO,Cy_3O_3$. This salt, heated in the dry state, evolves hydrated cyanic acid. If a solution of silver be added to a boiling solution of cyanurate of ammonia, containing ammonia in excess, the cyanurate with 3 atoms of oxide of silver, is formed: $3(AgO)Cy_3O_3$.

ARSENITE OF SILVER, $2(AgO)AsO_3$, is precipitated in the form of a pale yellow powder, soon becoming deeper yellow, gray, and brown, by the addition of arsenite of potassa, to nitrate of silver. Arsenious acid only produces a white cloud in solution of nitrate of silver, but the yellow arsenite falls on the subsequent addition of a small quantity of alkali. This salt retains its yellow color when carefully dried, but becomes brown on exposure to light.

ARSENATE OF SILVER, $3(AgO)AsO_5$, is thrown down from nitrate of silver by arsenic acid, and by the soluble arseniates, of a reddish-brown color. It is insoluble in water, but soluble in aqueous ammonia; it dissolves in nitric acid, and in acetic acid.

CHROMATE OF SILVER, AgO,CrO_3, is precipitated of a crimson color by mixing solutions of chromate of potassa and nitrate of silver. It soon loses its brilliant tint and becomes brown.

BICHROMATE OF SILVER, $AgO,2CrO_3$ is precipitated by adding bichromate of potassa to an acid solution of nitrate of silver. When boiled in water it is resolved into dark green neutral chromate, and an acid solution, which, on cooling, again deposits crystals of bichromate.

ALLOYS OF SILVER.—The compounds of silver with *potassium*, *sodium*, and other light metals, have not been examined. When silver and *steel* are fused together, an alloy is formed, which appears perfect while in fusion, but globules of silver exude from it on cooling, which shows the weak attraction of the metals. At a very high temperature, the greater part of the silver evaporates, but a portion equal to about 1 in 500 remains, forming an alloy known as *silver-steel*, and said to be well adapted to the formation of cutting instruments, but subject to rust from galvanic action. Silver readily combines with *zinc*, producing a brittle bluish-white granular alloy. With *tin* silver forms a white, hard, brittle alloy. The alloy with *copper* constitutes plate and coin. By the addition of a small proportion of copper to silver, the metal is rendered harder and more sonorous, while its color is scarcely impaired. When the two metals are in equal weights the compound is white: the maximum of hardness is obtained when the copper amounts to one-fifth of the silver. The *standard silver* of this country is composed of 92·5 silver+7·5 copper; that of France, of 90 silver+10 copper; and in that of Prussia, the alloys amount to 25 per cent. The specific gravity of British standard silver is 10·3. The silver coins of the ancients, and many

Oriental silver coins, are nearly pure; they only contain traces of copper and of gold. When silver alloyed by copper, such as standard silver, is exposed to a red heat in the air, it becomes black from the formation of a superficial film of oxide of copper; this may be removed by immersion in hot diluted sulphuric acid, and a film of pure silver then remains, of a beautiful whiteness: this is called *blanched*, *dead*, or *frosted silver*. The blanks for coin are treated in this way before they are struck, whence the whiteness of new coin, and the darker appearance of the projecting portions occasioned by wear, in consequence of the alloy showing itself beneath the pure surface; articles of plate are often deadened, *matted*, or *frosted* by boiling in bisulphate of potassa (*sal enixum*), which acts in the same way as dilute sulphuric acid. *Lead* and silver form a very brittle dull-colored alloy, from which the lead is easily separated by cupellation. When fused lead containing silver is suffered to cool slowly, the lead, which first concretes, forms granular crystals, and is nearly pure, while almost the whole of silver is contained in the liquid portion; in this way the separation of the two metals may to a certain extent be effected, especially upon the large scale (p. 26). *Antimony* forms a brittle white alloy. With *Bismuth*, the alloy is brittle and lamellar. When silver and *arsenic* are fused together, an alloy is formed, which, is gray, brittle, and granular. Silver amalgamates easily with *mercury:* when red-hot silver is thrown into heated mercury it dissolves, and when 8 parts of mercury and 1 of silver are thus combined, a granular crystalline soft amalgam is obtained. When a solution of this amalgam in liquid mercury is squeezed through chamois leather, the excess of mercury, retaining only a trace of silver, goes through, and the solid amalgam is left behind. Amalgam of silver is sometimes employed for *plating;* it is applied to the surface of copper, and the mercury being evaporated by heat, the remaining silver is burnished. The better kind of plating, however, is performed by the application of a plate of silver to the surface of the copper, which is afterwards extended by rolling. A mixture of chloride of silver, chalk, and pearlash, is employed for silvering brass: the metal is rendered very clean, and the above mixture, moistened with water, rubbed upon its surface. Plating by metallic precipitation from ammonio-chloride of silver is also frequently resorted to, but *electro-plating* with cyanide of silver, now supersedes the other methods.

ASSAY OF SILVER.—The analysis of alloyed silver is in continual practice by refiners and assayers. It may be performed in the humid way by dissolving the alloy in nitric acid, precipitating with hydrochloric acid or chloride of sodium, and either reducing the chloride, or estimating the quantity of silver which it contains; every 100 parts of the carefully dried chloride indicating 75·33 of silver.

But a modification of this method is now generally resorted to, especially applicable in cases where the quality of the alloy is approximately known: it depends upon the precipitation of the silver by a *standard solution of common salt*, each 1000 grains of which contain a sufficient quantity of salt to precipitate 10 grains of silver; so that, supposing the silver and the salt to be pure, 10 grains of silver dissolved in nitric acid, would be entirely precipitated by 1000 grains of the standard solution. To effect this, each 1000 grains of the standard solution must contain 5·55 grains of pure chloride of sodium; this is equivalent to 388 grains in each gallon of such solution; but as commercial salt is not absolutely pure, the exact strength of the standard solution must be experimentally adjusted by dissolving 10 grains of perfectly pure silver in nitric acid, precipitating it by 1000 grains of the solution, and adding either salt or water, as may be required. Having thus prepared this standard solution of salt, 1000 grains of it are put into a convenient counterpoised burette, or dropping-bottle; 10 grains of the sample of silver to be assayed are then placed in a stoppered bottle capable of holding about 6 ounces of water, and dissolved in about 2 drachms of nitric acid of sp. gr. 1·25. Such portion of the solution of salt is then added as will be required to throw down *nearly* the whole of the silver; the bottle is then well shaken for about a minute, and the precipitated chloride allowed to subside. When the liquor above it has become clear, a drop or two more of the standard solution is added, and if it occasions any precipitate, the bottle is again shaken, and, when clear, more of the standard solution is very cautiously added, as long as it occasions any turbidity. When no cloud is produced, the weight of the standard solution which has been added is ascertained by re-weighing the burette, and the number of grains so employed indicates the quantity of pure silver in the sample: if this be of the fineness of English standard silver, 925 grains of the standard solution will have been used, indicating the composition of the alloy to be 9·25 silver and 0·75 copper: if the sample be of the French standard, 900 grains of the salt solution will have been required, indicating an alloy of 9 silver and 1 copper. This process of humid assaying was introduced into the French Mint by Gay-Lussac, who has described it in detail, together with the apparatus required for carrying it out, and the precautions necessary to insure accuracy. A full description of this method, by Mulder, will be found in the *Chemical News*, 1861, vol. 2, pp. 137—204.

Assayers generally determine the value of silver bars by the process of *cupellation*. Of the useful metals, three resist the action of air at high temperatures—namely, silver, gold, and platinum; the others, under the same circumstances, become oxidized: it might, therefore, be supposed, that alloys of the first three metals would suffer decomposition by mere exposure to heat and air, and that the oxidizable metal would burn into oxide. This, however, is not the case: for if the proportion of the latter be small, it is protected by the former; or, in other cases, a film of infusible oxide coats the fused globule, and prevents the further action of the air. These difficulties are overcome by adding to the alloy some easily oxidizable metal, the oxide of which is *fusible*. Lead is usually selected for this purpose. Supposing, therefore, that an *alloy of silver and copper* is to be *assayed*, or analyzed by *cupellation*, the following is the mode of proceeding: A clean piece of the metal (about 20 grains) is laminated, and accurately weighed. It is then wrapped in the requisite quantity of *pure* sheet-lead, apportioned by weight to the *quality* of the alloy, and placed upon a small *cupel*, or porous shallow crucible, made of bone-earth. The whole is then placed within the *muffle*, heated to bright redness: the metals melt, and, by the action of the air which plays over the hot surface, the lead and copper are oxidized, and their fused oxides are absorbed by the cupel, and, if the operation has been skilfully conducted, a button of pure silver ultimately remains, the completion of the process being judged of by the cessation of the oxidation and motion upon the surface of the globule, and by the brilliant appearance assumed by the silver when the oxidation of its alloy ceases. The button of pure silver is then suffered to cool gradually, and its loss of weight will be equivalent to the weight of the alloy which has been separated by oxidation, a certain allowance being made for a small loss of silver, which always occurs, partly by evaporation, and partly by the metal being carried off with the oxides which are absorbed by the cupel. To perform this process with accuracy, certain precautions are requisite, which can only be learned by practice, so as to enable the operator to obtain uniform results.

TESTS FOR THE SALTS OF SILVER.—1. The soluble salts of silver give with hydrochloric acid, and with soluble chlorides, a white curdy precipitate, which is readily soluble in ammonia and in hyposulphite of soda, but insoluble in nitric acid: it darkens by exposure to light. 2. With the fixed alkalies brown precipitates are produced, insoluble in the excess of the alkali. 3. With ammonia the precipitate is also brown, but readily redissolves in an excess of the precipitant. 4. With sulphuretted hydrogen and hydrosulphate of ammonia, the precipitate is black and insoluble. 5. Protosulphate of iron throws down metallic silver. 6. A yellow precipitate with common phosphate of soda, and with arsenite of potassa, a brick-red precipitate with arsenate of potassa, a crimson with chromate of potassa, and a white with ferrocyanide of potassium, are further characteristics. The silver salts insoluble in water are mostly soluble in ammonia, and in nitric acid. These salts, excepting those containing colored acids, are either white or of a pale yellow color, provided they have not been exposed to light, to sulphuretted hydrogen, or deoxidizing agents. Many of the metals, especially copper, tin, and lead, separate metallic silver when immersed in its solutions. Before the blowpipe the silver salts are easily reduced, especially when mixed with carbonate of soda.

CHAPTER XXXIX.

PHOTOGRAPHY AND ITS APPLICATIONS.

THE CHEMISTRY OF LIGHT.

THE art of photography is based on the chemical changes which the salts of silver undergo, when exposed to light. Silver is not the only metal which is affected by light. Solutions of gold in contact with organic matter, yield metallic gold of a deep purple color. The compounds of mercury, chromium, uranium, iron, and molybdenum, are either reduced to a lower state of oxidation by light, or, as in the black oxide of mercury, the metal is set free. But there are no metallic salts which are so favorable for the practice of photography as those of silver; hence they are almost exclusively employed for this purpose.

In some cases, a pure binary compound of the metal, AgI, or AgBr, is used on a surface of metallic silver, as in the *daguerreotype* process: in others, a binary salt, obtained by double decomposition, associated with pyroxyline, is selected, as in the *collodion* process. The silver-compound used with *dry* collodion, is the same as that of the daguerreotype, namely, AgI, or AgBr, and is frequently a compound of the two; while with the *wet* collodion, there are not only these two salts, but free nitrate of silver. In the ordinary *paper* process, the chloride of silver (AgCl) is employed; but there is associated with this, free nitrate of silver; and when the surface of the paper is albuminized, an organic compound of albuminate of silver.

All the salts of silver are more or less affected by light. In some instances they undergo a visible change, being rendered dark in proportion to the intensity of the light and the length of exposure. This is well seen in the white chloride of silver when in a humid state; and in the nitrate and ammonio-nitrate in contact with organic matter. It is less apparent in the sulphocyanide, the hyponitrite, and pyrophosphate of silver, and is scarcely visible in the cyanide, even after long exposure. The iodide and bromide of silver do not darken by exposure to light, but they undergo instantaneously a remarkable molecular change, which renders them especially adapted for photography.

The conditions necessary for these changes are light, and moisture. When the salt of silver is in contact with albumen or gelatine, the reduction is not only accelerated, but it takes place with greater uniformity and depth. A decomposable salt of silver in contact with organic matter, will spontaneously change in the dark in a humid atmosphere; and thus it is well known that paper employed in photography, when once sensitized, or impregnated with a silver solution, cannot be preserved unless certain precautions are taken. The albuminate and chloride of the metal, formed upon the surface of the paper in the act of sensitizing it, are decomposed, and the paper is slowly darkened. The effect of a dry atmosphere in preserving the salts of silver from change has been elsewhere described (p. 41). As pure *chloride of silver* undergoes no change of color when exposed to light in an atmosphere artificially dried by chloride of calcium, the presence of water or moisture appears to be necessary to the change; but the presence of organic matter is not absolutely necessary. In contact with water alone, the chloride changes from a snow-white to a pink, violet, brown, and finally a dark bronze-black color; and during this conversion, hydrochloric acid is produced. Hence the chemical change may be thus represented: $AgCl+HO=Ag+HCl+O$. According to Mitscherlich, the precipitated chloride, well dried, inclosed in a tube, and exposed to light, is decomposed, and chlorine only liberated: $AgCl=Ag+Cl$. The darkening of a layer of the precipitated chloride is superficial; if the surface be removed, the chloride beneath will be found quite white. When the chloride is precipitated on paper for photographic purposes, the change, after long exposure, extends more or less into the substance of the paper. If ammonia is poured upon the precipitated chloride which has been exposed to light, that portion which has not undergone the change, is dissolved, while the dark substance (*i.e.*, the reduced silver) remains undissolved. If a strong solution of chlorine is added to the darkened chloride, it is again rendered white, by reason of the metallic silver recombining with this element; and the white chloride, when covered with a solution of chlorine, does not readily undergo the change. A solution of common salt or hydrochloric acid in excess, also retards the change; but when the solution of nitrate of silver is in excess, it takes place with very great rapidity. We have preserved paper prepared with chloride of silver, but containing an excess of chloride of sodium, for a period of twenty-two years. Under strong solar light it retained after this long interval, sufficient unchanged chloride, to yield an impression from a collodion negative.

Nitrate of silver undergoes no change by exposure to light, except when in contact with organic matter: the nitric acid and oxygen are then liberated, and the silver is reduced; $AgO,NO_5=Ag+O+NO_5$. The oxygen is probably taken by the hydrogen and carbon of the organic matter. The insoluble chloride, iodide, and bromide of silver are not so readily decomposed, when in contact with organic matter in the dark, as the soluble nitrate, or the ammonio-nitrate of silver. If mixed with the nitrate, however, they rapidly undergo a change: hence, for the perfect preservation of plates or paper covered with iodide of silver, it is necessary that every trace of the nitrate of silver should be removed. On this principle is founded the *dry-plate* process in photography. The dry and pure iodide of silver, free from nitrate, will receive an impression on exposure, just as certainly, although not so rapidly, as the wet iodide mixed with nitrate. Among the facts which prove that the chloride and nitrate of silver, are reduced by light to the metallic state, are the following: 1. The substance which has been darkened by light is insoluble in ammonia and the alkaline hyposulphites; while that portion of the salt of silver which has not undergone the change, is readily dissolved by these reagents. 2. When the reduction of the chloride or nitrate has taken place on paper, the surface has been found to conduct electricity. 3. When paper which has thus been darkened by light is introduced into a weak solution of chloride of gold, rendered slightly alkaline, metallic gold is slowly deposited of a dark purple color, in place of the reduced silver; an effect similar to that produced by metallic silver when immersed in a solution of gold. The well-known process of *toning* photographs, depends on this property of chemically replacing silver by gold: and there is but little doubt that the impressions are thus rendered much more durable. It is an ascertained fact, that this replacement, or substitution, does not occur except in those portions of a drawing, in which the silver has been completely metallized, or reduced by light.

There is another circumstance connected with this metallization of silver, under the influence of light, which is deserving of notice. When all other conditions are favorable, the rays of the spectrum affect the salts of silver unequally. If paper, containing the albuminate and chloride of silver, is covered with plates of glass variously colored, and is then exposed for an equal time to light, it will be found that under some of the dark-colored plates the change has been nearly as great, as if colorless glass had been employed, while under the lighter-colored plates, it has been retarded. Experiments of this nature have clearly proved that the dark or more refrangible rays of light, violet, indigo, and blue, allow the chemical changes to take place rapidly; while the less refrangible rays, red, orange, and yellow, retard them. Of all the colors, the blue produces, within a given time, the greatest, and the red, the least amount of chemical action. Thus the sensitized paper is intensely blackened under blue glass, while it remains nearly white under red glass. In no instance, however, are the chemical rays completely intercepted; for a long exposure will slowly lead to a change of color in the paper. The chemical action of light is therefore determined by the difference between the accelerating and retarding rays, of which white light is constituted. Colorless light, however, produces, *cæteris paribus*, a more rapid and complete change than the isolated blue rays of a colored medium.

From these facts it will be perceived that the two ends of the solar spectrum, do not neutralize each other in reference to this force; for the *actinic* or *chemical* rays predominate, and are found to operate sooner or later through every color. Nothing but the absolute withdrawal of light will entirely arrest the chemical changes. Hence the salts of silver may be employed for photometric observations. They serve to measure, not only the relative intensity of light, but by the changes induced on sensitized paper, they are made available for numerous important purposes in science and the arts. We have thus seen this art successfully applied to the diurnal registration of the amount of rain-fall; the electrical tension of the atmosphere, and the force and direction of the wind. It has also furnished important evidence in Courts of law, and has been usefully employed to illustrate various subjects in medicine, natural history, archæology, ethnology, and astronomy.

Other conditions connected with these phenomena are worthy of notice. The chemical changes produced in the salts of silver are not in proportion to the illuminating power of the rays of the spectrum. The greatest amount of light is in the yellow rays, and the least amount in the blue and violet; but the latter possess the chemical power in its greatest intensity. The salts of silver, it is well known, are decomposable by heat: but in reference to these changes, it is found that the calorific rays (red) have the least influence in producing them. Hence, this photochemical force is not in proportion to the light or heat of the solar rays, but to other rays which are called *actinic;* and the force itself is therefore called *actinism.* In reference to the spectrum, it is at its maximum when the violet and blue rays predominate, and at its minimum when the yellow and red rays are most abundant. Hence, if red or yellow rays abound, as in a glowing sunset, or occasionally in a foggy state of the atmosphere, however clear an image may appear to the eye, the actinic power is lost, and an impression cannot be taken.

The salts of silver differ from each other in respect to the changes produced by colored light: thus while the maximum effect on the chloride paper is in the blue rays, that produced on the iodized paper is in the extreme violet, while the bromized paper is affected more or less throughout the whole spectrum, even in the yellow and red rays. These remarkable effects produced by the colored rays of the spectrum, have not received any explanation on the undulatory theory of light: and it seems difficult to understand how an undulation, or any mechanical vibration, producing a violet color, should break up the chemical composition of chloride of silver, while that which produces a yellow or red ray, should have little or no effect upon this salt.

The colored rays of the spectrum are represented on prepared paper by degrees of darkness, or a blackening of the exposed portions, and not by the reproduction of *color.* It has been hitherto found impossible to procure and fix, by the chemical agency of light, the colors of external objects. We have in one instance seen the iridescent colors of the opal transferred to a surface of silver, by the daguerreotype; but they entirely disappeared on the preservation of the impression. Further, the unequal action of white light as it is reflected from white surfaces, as well as from shadows and shades of various degrees, is so great, that it is difficult, if not impossible, to attain the even gradation of tone which gives harmony to all natural objects. White light acts with such disproportionate rapidity, and the light of shadows so slowly, that the most finished impressions of objects are generally left with extremes of light and shade. While the lights are unnaturally intense, the shadows are generally black, without that gradation which in nature serves to reveal the most minute details. To a certain extent, this defect is, however, remediable by art.

With a knowledge of the principles above described, a chemist may produce, and render permanent, images which have been impressed by light on a salt of silver. He may select a medium of metallic silver, glass, or paper, and he may produce the image on the prepared surface, either by refraction with a camera obscura, or by superposition and simple exposure to diffused light. In either case he may obtain, directly or indirectly, an image in metallic silver, in those parts in which the metal has been reduced; while the undecomposed salt of silver remains in those spots, in which there has been a deficiency or entire absence of light. A solvent is selected for the removal of the unchanged salt, and the drawing is thus preserved.

The fact that images of objects might be impressed by light on *paper*, impregnated either with the chloride or nitrate of silver, had been proved experimentally by Davy and Wedgwood in 1802; but they could discover no method of fixing or preserving them. It was not until 1816, that the solvent properties of the alkaline hyposulphites on the salts of silver, were first made known; but so slow was the progress of this subject, that even in 1839, Mr. Fox Talbot, in announcing his discovery, could suggest no better means for the preservation of his drawings, than the use of strong solutions of alkaline chlorides, iodides, and bromides, which were soon proved to be quite inefficient.

1. DAGUERREOTYPE. *Photography on Silver.*—This branch of the art has received its name from the discoverer, Daguerre, who first announced his

process in the year 1839. This may be regarded, in a chemical point of view, as photography in its most simple form. A highly polished plate of silver is exposed to the diluted vapor of iodine, in a dark box. A colored film of iodide of silver (AgI) is thus produced by direct combination, and this, at a certain stage, is found to possess a high degree of sensitiveness to light. The use of bromine in addition to iodine was suggested by Mr. Goddard in 1840. A compound film of bromoiodide of silver was thus produced; and this is found to give more satisfactory results than the iodide alone. The plate is then transferred from the dark room to a camera, and in from five to ten seconds it is removed. In this stage nothing is visible on the plate. The film has the same bronze-yellow color, as when it was placed in the camera; but a molecular change may be proved to have taken place. When the plate is exposed in a box, at a moderate temperature, to the vapor of mercury, an image will immediately appear, the metallic vapor fixing itself closely (by amalgamation) only on those parts which have received the luminous impression, the mercury lying loosely on the other portions without entering into chemical combination. When a strong solution of an alkaline hyposulphite is poured over the plate, the image appears in full relief, with a contrast of light and shade, and with the most delicate details. The portions of bromoiodide of silver not acted on by light, are dissolved by an alkaline hyposulphite; and the highly polished silver beneath, forms the deep shades, which give blackness to the picture. The mercury imparts a dull white appearance to those parts of the metal with which it is chemically combined or amalgamated, and thus constitutes the lights.

The action of light on the bromo-iodide of silver, probably consists in displacing the bromine and iodine, wholly or in part, and thus leaving a metallic surface favorable for combination with the vapor of mercury: ($Ag,Br = Ag + Br$). Mercury does not combine with the salts of silver: hence, the film of undecomposed bromo-iodide in those parts which were not exposed to light, is sufficient to prevent any direct union between the mercury and the silver beneath. After the undecomposed salt of silver has been removed by the alkaline hyposulphite, the plate simply requires washing. A film of gold may be then spread over it by heating upon its surface a layer of a very diluted solution of chloride of gold in hyposulphite of soda; and another washing completes the operation.

Owing to the highly polished surface of the metal, the daguerreotype is admirably adapted to bring out the minutest details of objects. In 1846 we obtained by this process a copy of the 10,000 letters of the Greek inscription on the Rosetta stone of the British Museum, within the space of two square inches. The drawing is still preserved, and the Greek letters are easily legible by the aid of a lens. The process, however, has these disadvantages: the film is so thin that the polish of the silver prevents the image from being clearly seen in all lights; and, as with all silver-surfaces, the plate is exposed to tarnishing by sulphuration. These drawings therefore can only be preserved by completely preventing the access of air.

2. THE COLLODION PROCESS. *Photography on Glass.*—The application of pyroxyline, or gun-cotton, to the purposes of photography, was discovered by Mr. Archer, in 1850. It is used either in the wet or dry state; and as it is employed on glass, it may be applied either for the production of *positive* images, with the light and shade correct; or of *negative* images, in which the light and shade are reversed. Positive impressions on paper may be procured from the latter. Collodion is a solution of pyroxyline in a mixture of ether and alcohol. (*See* PYROXYLINE.) There are several compounds known under the name of gun-cotton, but one of these only appears to be well fitted for photographic purposes (p. 160). It is what is called a

substitution-compound, in which, assuming cotton to be $C_{24}H_{20}O_{20}$, four equivalents of nitrous acid are substituted for four of hydrogen, thus bringing the formula of photographic cotton to $C_{24}[H_{16}4(NO_4)]O_{20}$. The proportion of cotton to the mixed solvents, varies according to circumstances. From 5 to six grains of cotton may be used to an ounce of a solvent consisting by measure of one part of alcohol (sp. gr. 0·830) and two parts of ether (sp. gr. 0·724), the latter being diminished, and the former increased, in hot weather. When the collodion is required for use, it is necessary to add to it an alcoholic solution of an iodide, either of potassium, cadmium, or ammonium, or a mixture of these. The proportion of iodide required, is from 4 to 6 grains to each ounce of collodion. Pure iodide of potassium, free from iodate (*see* page 299), is commonly selected for immediate use; and the iodide of cadmium when the liquid is required to be preserved. A mixture of equal parts of the two, *i. e.* 2½ grains of each iodide, dissolved in 2 drachms of alcohol, will be found convenient. This quantity may be added to 6 drachms of the prepared collodion. A mixture of the iodides of potassium, ammonium, and cadmium is frequently employed with advantage; and an addition of the bromide of either metal to the iodide, renders the film more sensitive to the less refrangible rays of light (yellow and red) (page 471.) In using a bromide, the proportion should not exceed 1 to 3 or four parts of the iodide. Reynaud advises for each ounce of collodion 5·3 grains of iodide to 1·5 grains of bromide, as producing the most sensitive film. The bromides of ammonium and cadmium are, according to him, preferable for this purpose.

When collodion thus prepared, has been rendered perfectly clear by subsidence, it is poured rapidly from a wide-mouthed vessel over a freshly cleaned and dry surface of plate-glass; and as soon as it is set into a coherent layer, the glass is plunged into a bath containing a solution of nitrate of silver, in a darkened room.

This bath is prepared by dissolving 480 grains of neutral crystallized nitrate of silver in 2 ounces of water, and adding to the solution 4 grains of iodide of cadmium or potassium, dissolved in a small quantity of water. Iodide of silver is thus formed, and dissolved by the concentrated nitrate. The solution may be then made up to twelve fluid ounces, by the addition of distilled water. After standing some hours, it should be filtered to separate the precipitated iodide of silver. The solution when filtered, should neither be alkaline nor neutral. If acid, a little oxide of silver may be used to correct this; and when corrected, it may be very slightly acidulated, either with a few drops of glacial acetic acid, or of strong nitric acid (containing nitrous acid) properly diluted. If the bath is neutral, the pictures are not clear; if too acid, the sensitiveness of the film is impaired. To avoid a "fogging" of the impression, it has been lately suggested that a few drops of an alcoholic solution of iodine, should be added to the bath-liquid, until it has acquired an orange-yellow color. (Reynaud).

The result of the immersion of the plate in this bath for a few minutes, or until the oily appearance of the film is removed, is the production in it, of a primrose-colored layer of iodide of silver, while nitrate of soda or cadmium is dissolved in the bath: $(AgO,NO_5+KI(CdI)=AgI+KO(CdO)NO_5)$. If, when taken from the bath, the opaque yellow film is well washed, to remove all traces of free nitrate of silver, it may be dried, and the dry plate preserved in a sensitive state in a dark box (containing some quick-lime) for many weeks, or even months. We have thus obtained impressions on dry plates after four or five months' preservation. The absence of moisture and the entire withdrawal of light are, however, essential conditions for the preservation of the plates. Various liquids, such as tannic acid, albumen, and a solution of chloride of sodium, have been employed as varnishes for covering and preserving the film, containing the precipitated iodide of silver.

The plate with the iodide of silver on its surface, may be exposed in the camera for a few seconds if wet, and for a longer period if dry. When removed, no image is perceptible; but on pouring over the film of iodide, a solution of gallic or pyrogallic acid, or of a protosalt of iron, mixed with a few drops of a weak solution of nitrate of silver, the image will appear, slowly or rapidly according to the nature and strength of the developer, the degree of exposure, and the intensity of light. The developing solution, as it is called, may be thus prepared: One grain of pyrogallic acid, thirty minims of alcohol (to cause the liquid to flow freely over the surface), and thirty minims of glacial acetic acid, or (in place of the acetic) two grains of citric acid are dissolved in one ounce of water. If the temperature is low, the proportion of pyrogallic acid may be increased to one grain and a half, and the citric acid reduced to one grain. The dry plate should be breathed upon, or wetted with distilled water, before the developing solution is poured over it, in order that the latter may be readily diffused over the whole surface. The illuminated portions of the picture will appear, under the action of the reducing liquid, more or less black, while the shaded portions will retain the yellow color of the iodide. When the details of the shaded portions appear, the acid liquid is washed off, and the development is arrested. The surface of the plate is then well washed, and covered with a *saturated* solution of hyposulphite of soda. After a few minutes, it will be found that the yellow iodide of silver, where it has not been affected by light, will be dissolved; and only the reduced or metallized portions of silver will remain: these appear more or less opaque when viewed by transmitted light. The plate now requires the most complete washing to remove every trace of hyposulphite of soda, or the film of reduced silver will be subsequently cracked and destroyed by the crystallization of traces of this salt beneath.

The changes which take place in the production of the image on the iodide of silver, have been variously explained. All agree that the effect of the impingement of light, is to produce only a *molecular* change in the compound. There is no perceptible alteration in the film after exposure to light. There is no loss of iodine, or the iodide would be darkened like the chloride. The film retains its chemical properties, and whether on paper or on silver, it is still easily dissolved by the alkaline hyposulphites. In reference to the Daguerreotype, a molecular change in the iodide, is proved to exist, by the vapor of mercury fixing itself only on those parts which have been exposed to light, excluding the iodine and combining directly with the metallic silver. In regard to the collodio-iodide, it may be inferred from the effect of reducing agents, that the changes consist in a deoxidation of the nitrate and a deiodization of the iodide of silver. It is a singular fact, that while a molecular change is produced in the iodide by the agency of light only, the actual production of the image depends on the presence of a small quantity of nitrate of silver, either on the plate itself in the wet process, or by an addition of it to the reducing liquid in the dry process.

The effects produced by reducing agents, such as the gallic and pyrogallic acids, on the oxysalts of silver, are somewhat remarkable. Gallic acid reduces a solution of the nitrate very slowly at common temperatures: pyrogallic acid reduces it instantaneously, throwing down black metallic silver by taking the oxygen from the oxide: $(AgO,NO_5+C_{12}H_6O_6=Ag+NO_5+C_{12}H_6O_6,O)$. A solution of the sulphate of silver is scarcely changed in color by the gallic, and is only slowly decomposed by the pyrogallic acid.

When acetic or citric acid is mixed with the pyrogallic, the reducing action is retarded, much more by the citric, than by the acetic acid. It is in order to prevent a too rapid decomposition, by which the plate would be speedily covered with precipitated silver, and the picture rendered indistinct, that one or other of these acids is added to the reducing liquid. Either of them has the property of lowering the reducing power of the pyrogallic even to that of the gallic acid. On the other hand, the presence of any alkali leads to the instantaneous decomposition of a salt of silver. Thus, when pyrogallic acid is added to a solution of the ammonia-nitrate of silver, the metal is immediately reduced and precipitated. It has been elsewhere stated that a solution of pyrogallic acid in potassa has the property of entirely removing oxygen from air (p. 141). Neither the gallic nor the pyrogallic acid exerts any reducing action on the chloride, bromide, or iodide of silver, except in the presence of an excess of nitrate, when both the oxysalt and haloid compound are decomposed. The decomposition appears in all cases to commence with the nitrate and to extend to the iodide; but unless the iodized film has been exposed to light, it resists the action of pyrogallic acid, even in the presence of nitrate of silver. The proportion of nitrate in the reducing liquid, is commonly greater than that of the pyrogallic acid employed. It is another curious feature of these changes, that when once the silver has been reduced as a result of the impression of light, a continued reduction of the nitrate of silver by a further employment of this salt mixed with pyrogallic acid, does not obscure the image, or produce a loose deposit over the whole surface of the plate. The fresh portions of silver as they are set free by the pyrogallic acid, fix themselves upon the metal already reduced, add to its thickness, and thus increase the intensity of the darkened portions. The fact is well illustrated in the process of *intensifying* a negative, in which the reduced metal forms a basis for an increased deposit of metallic silver from the nitrate. This depends on the well-known principle, that like particles attract each other in preference to unlike. The reduced silver coheres to the metallic silver of the film, but not to the layer of undecomposed iodide.

Pyrogallic acid rapidly deoxidizes strong nitric acid, but it has no action on it in the very diluted state in which the latter is here liberated; and it has no tendency to decompose the iodide of silver alone; but assuming that the molecular condition of the iodide has been broken in the parts which have received an impression from light, it is probable that the iodine is thereby placed in a state for removal by very slight causes. As the result of the application of the reducing agent is the same, whether it is employed immediately or after eighteen hours (if the plate has been kept in the dark), it is clear that this molecular displacement of the atoms of silver and iodine, is not of a temporary kind, or the power of bringing out the image would be speedily lost. The iodide on the plate, in the parts affected by light, may be decomposed by the metallic silver which is liberated from the nitrate by pyrogallic acid, so that the same compound may be decomposed by light, and reformed by the reducing agent. If the compound on the plate after the action of light, is represented by AgI, and the silver liberated from the nitrate by the pyrogallic acid be regarded as Ag, then the change would be as in the following equation, $AgI, + \mathrm{Ag} = \mathrm{Ag}I + Ag$. The iodine is removed from the iodide, and it must be removed either as iodide of silver (AgI), or (on the assumption that water is decomposed) as hydriodic acid (HI), the oxygen of an atom of water being taken by another portion of the pyrogallic acid. The last view is entirely opposed to the fact that pyrogallic acid with water, has no decomposing action on the iodides, whether soluble or insoluble in water. A solution of iodide of potassium is not decomposed by pyrogallic acid. A solution of iodine in water does not lose its color by the addition of this acid, although it is so changed that starch will no longer render it blue. Hence, under the most favorable circumstances, water is not decomposed by pyrogallic acid in the presence of a metallic iodide.

In place of pyrogallic acid, or the protosulphate of iron, the protonitrate of uranium is sometimes employed as a reducing agent. The protosulphate of iron passes to the state of persulphate at the expense of the oxide of silver. $3(FeO,SO_3)+AgO,NO_5=Ag+Fe_2O_3,3SO_3+FeO,NO_5$ (p. 468). It is employed in the proportion of 14 grains to the ounce of water, acetic acid and alcohol being added in the proportions above given. This reducing agent produces less dense negatives: the reduced silver assumes a white crystalline or frosted state, and the more acid the sulphate from the presence of free sulphuric or nitric acid, the stronger is this effect. There is another evil attending its use—the silver is frequently reduced to a metallic film on the surface of the liquid; this falls on the collodion-negative, and cannot be removed by mere washing. The image is thus obscured. The sulphuric may be replaced by the acetic acid, as in adding acetate of lead or acetate of baryta to a solution of the protosulphate of iron, and filtering the liquid. Nitrate of baryta has been employed for a similar purpose, and in this case nitric acid is set free. The iron-developer should always be strongly acid (with acetic acid) in order to prevent a too rapid reduction of the salt of silver. The addition of acetic ether and hyponitrous ether has been found to operate effectually in a similar manner. Like the pyrogallic acid, the protosulphate of iron has no action on the iodide of silver unless free nitrate is present, and unless the iodide has been exposed to light. It does not decompose either the soluble or insoluble iodides, and it does not discharge the color of a solution of iodine, or prevent the formation of the usual blue compound on the addition of a solution of starch.

The reduced silver on the plate is insoluble in a solution of hyposulphite of soda, but the undecomposed iodide is dissolved by it. It forms a compound salt with the iodide: its action may be thus represented: $AgI+2(NaO,S_2O_2)=NaI+NaO,AgO,2S_2O_2$. The glass plate thus preserved may, according to the degree to which the image has been brought out, be employed as a *positive*, by placing it on a dark background, in which case those portions that are opaque to light, or in which the silver is deposited, will reflect light, and furnish the lights of the picture; while those which are transparent, and on which the light did not act, will appear black from the nature of the background, and these will represent the shadows of the picture. In the Daguerreotype the picture is inverted when finished, while in the collodion positive it appears non-inverted. In a further stage of development, the image may be so strongly defined that the deposited silver will more or less completely intercept the light, producing a negative impression, from which a non-inverted image, or positive drawing, may be procured on another sensitized surface. In order to protect the film on the plate from injury, it is necessary to varnish the collodion side with amber or resinous varnish. The former is preferable, as it is not softened by solar heat in taking a positive drawing.

Recent experience has shown that the best method of proceeding for bringing out an image, is to employ a solution of protosulphate of iron in the first instance, and pyrogallic acid with nitrate of silver, subsequently. This produces a strong deposit of silver in the parts reduced by the sulphate. All traces of the solution of iron should be previously removed by washing. The image may be even thus intensified by pyrogallic acid after the removal of the unchanged collodio-iodide of silver by hyposulphite of soda, care being taken that no traces of this salt remain on the glass plate.

3. PHOTOGRAPHY ON PAPER.—In 1839, Mr. Fox Talbot first published a method of procuring images on paper with the salts of silver, and of so preserving them, that from the negatives, positive drawings (in which the light and shade were correct), might be taken by superposition and exposure. He used the chloride, iodide, or bromide of silver; and various saline solutions as preservatives. He gave to one modification of his process for producing the image the name of *Calotype.* In this, the image was received on paper impregnated with iodide of silver, and afterwards developed by a mixture of gallic acid and nitrate of silver. It would be impossible here to describe the numerous modifications which the so-called paper-process has assumed, since it was first discovered. Owing to imperfect methods of preservation, nearly all the drawings which were taken at an early period, have perished. Paper impregnated with wax, with one part of wax to four parts of paraffin, with gelatin, albumen, and other substances, has been used, and admirable drawings of large size have been procured from transparent wax-negatives: but the paper-process is now chiefly confined to the procuring of positive impressions from collodion negatives on glass; and the salt of silver which is preferred for this purpose is the chloride ($AgCl$), with or without albumen, but always accompanied with free nitrate of silver.

Preparation of the Paper.—Paper manufactured for photographic use, should be floated for five minutes on a solution containing from 10 to 12 grains of chloride of sodium or ammonium to an ounce of water. When dried, it should be floated in a dark room, for another five minutes, on its salted surface, on a solution of nitrate of silver, consisting of from 60 to 80 grains to the ounce of water. When dry, it is fit for use. Paper prepared with a surface of albumen and impregnated with chloride of sodium, may be readily procured. This may be sensitized in a similar manner. A positive impression is taken by placing the collodion side of a negative plate, on which there is a fixed image, in contact with the dry sensitive side of the paper, and exposing it to light in a pressure-frame until the lights of the drawing are of a pale lilac hue, and the shades are of a deep bronze color. It is afterwards soaked in successive portions of tepid water, until the water is no longer rendered milky by the production of chloride of silver. It is then transferred to a *toning* bath, which is thus prepared: Bicarbonate of soda 1½ oz., water 90 oz.: dissolve and filter. A solution of chloride of gold should be so prepared as to contain 4 grs. of metallic gold to 1 oz. of water. (PERCHLORIDE OF GOLD, p. 480.) These solutions should be mixed, as they are required, in the following proportions: To 5 ounces of the solution of bicarbonate of soda, add 1 drachm of the solution of gold ($=\frac{1}{2}$ grain of metal). The drawing or drawings should be kept in motion, and remain in the bath until they have acquired a deep purple-black color. Those which are feebly printed will not acquire any depth of color; they become more faint. In fact, it is only in those parts in which the silver has been completely reduced by light, that this toning effect takes place. All the operations above described, except that of salting the paper, must be carried on in a darkened room. The drawing, after toning, should be washed in cold water, to remove any traces of the gold-bath, and then plunged for a quarter of an hour into a solution of hyposulphite of soda, containing 1 ounce of the salt to eight ounces of water. Any chloride of silver contained in the substance of the paper is thereby removed, while in a perfect drawing the color is but little changed, unless it is allowed to remain too long in the bath. It is now soaked in a large quantity of water, occasionally renewed, for twenty-four hours, with a view to remove all the compound hyposulphite of soda and silver. The last drainings of the drawing may be tested for any traces of hyposulphite, either by a solution of nitrate of silver, or of acid subnitrate of mercury. If any hyposulphite is still contained in the washings of the drawing, the former will give a brown color to the liquid, and the latter will produce a gray, or even a black precipitate.

In February, 1839, soon after the announcement of Mr. Fox Talbot's method of impregnating paper with chloride of silver, we found that a solution of ammonio-nitrate of silver gave greater certainty and uniformity in the results. The solution then called Photogenic liquid was prepared by dissolving 4 drachms of nitrate of silver in 6 ounces of water. Strong ammonia was added to the liquid until the oxide of silver at first precipitated was entirely re-dissolved ("On the Art of Photogenic Drawing," Jeffery. London, 1840, p. 6). The liquid was laid on the paper with a brush, the paper being selected according to the dark and even tone, which it acquired when prepared with the silver solution, and exposed to light. Drawings taken by this process, and preserved by the hyposulphite of lime, have undergone but little change in twenty-three years. The lights and shades are still well defined. In salting paper for the ammonio-nitrate of silver, the quantity of chloride of ammonium or sodium used, should be less than that employed for the nitrate. It was thought that such a solution would be dangerous for use, by giving rise to the production of fulminating silver; but having employed it with safety in large quantities for some years, and even after keeping it for a period of eight or nine years, it is evident that such a supposition is unfounded. The addition of a small quantity of alcohol and a few drops of nitric acid to the liquid, has been found to render it adapted for albuminized paper, the proportion of nitrate of silver employed, being about 70 grains to an ounce of water.

The chemical changes which take place in the various stages of the paper process may be thus described: Chloride of silver is produced in sensitizing the paper, $NaCl+AgO,NO_5=AgCl+NaO,NO_5$. The chloride is by this method of preparation evenly precipitated over the surface of the paper; but it is always mixed with free nitrate of silver, which accelerates and increases the chemical changes. When albuminized paper is used, in addition to the two preceding salts, an organic salt (the albuminate) is also produced. The three salts are decomposed by light, but in different degrees: the nitrate produces a brown-black, the chloride tends to produce a purple-black, and the albuminate a reddish-brown color, which is not easily darkened by the gold-bath. A deficiency of nitrate of silver in the silver-bath (as it is rapidly replaced by nitrate of soda), an undue proportion of chloride of sodium in the paper, or too short a contact with the sensitizing liquid, will affect the results. Exposure to light causes a reduction of the silver in the exposed parts to the metallic state: $AgCl=Ag+Cl$, and $AgO,NO_5=Ag+O+NO_5$; but only a very small portion of the silver salts on the paper is thus metallized. When the recent drawing is placed in tepid water containing an alkaline chloride, there is an abundant milky deposit, owing to the production of chloride of silver from the undecomposed nitrate in the paper. This should be removed as rapidly as it is formed, but the body of the paper will still hold a quantity, which surface-washing with water will not remove. When the drawing is now placed in an alkaline solution of gold, the gold is deposited either upon or in substitution of the metallic silver, giving to it a purple-black, in place of the red-brown color ($3Ag+AuCl_3=Au+3AgCl$), and rendering it better fitted to withstand the action of the hyposulphite of soda. A compound hyposulphite of gold and soda, which may be made by adding a weak solution of the chloride of gold to a concentrated solution of the hyposulphite, is preferable for the toning of drawings on plain salted paper. In this case it is, however, probable that the more perishable sulphide of silver still exists in the drawing, with precipitated gold. The perfect preservation of the drawing is based on two conditions: 1. The entire removal from the substance of the paper of any chloride of silver by the hyposulphite of soda: $AgCl+2(NaO,S_2O_2)=NaCl+NaO,AgO,2S_2O_2$. Hence the drawing should be left sufficiently long in this liquid, and it should be of a sufficient strength, but not greater than is required, for the removal of the chloride. If very strong, it injures the finer parts of the impression by dissolving the reduced silver. It is better, therefore, to employ a solution of the minimum strength for the removal of the chloride. If the solution is too weak it produces in the substance of the paper spots of brown sulphide of silver. 2. The second condition is, that the whole of the compound hyposulphite thus produced should be removed from the paper, otherwise it will undergo spontaneous decomposition, especially in a damp atmosphere. Brown and yellow stains sooner or later appear in the drawing, and thus destroy it. They arise from the decomposition of the hyposulphite of silver, which passes through a series of changes until it is resolved into sulphide of silver, and ultimately this appears to be itself resolved into sulphate of silver; ($AgO,S_2O_2=AgO,SO_2+S=AgS+SO_3$). The sulphuric acid probably reacts upon another portion of hyposulphite, forming sulphate of silver, and setting free sulphur and sulphurous acid. If the same solution of hyposulphite is too frequently employed, it becomes saturated with chloride of silver, forming apparently in the substance of the paper an insoluble double hyposulphite, which cannot be readily removed by washing. Hence a frequent renewal of the hyposulphite is required.

There are many points connected with the art of photography which can be acquired only by long practice. The causes of failure in every stage of the process are numerous, and are sometimes difficult of explanation.

CHAPTER XL.

GOLD. PLATINUM.

Gold ($Au=197$).

Gold has been known from the remotest ages: it is the *Sol* of the alchemists, who represented it by the circle ⊙, the emblem of perfection. It occurs in nature in a metallic state alloyed with silver or copper, and is called *native gold*. It is found disseminated in primitive or igneous rocks, or in the beds of rivers, and in alluvial deposits. The largest supplies have been derived from Australia and California; from Brazil, Mexico, and Peru; from the Ural Mountains; and from some parts of Africa. The rivers of Hungary, Transylvania, and Piedmont, have also yielded the metal; and it has been found in Cornwall, Wicklow, and North Wales. In 1861, the gold obtained from that principality is reported to have amounted to 2884 ounces. Gold has also been found in the refuse slags of sulphuric acid works, where pyrites has been used as a source of sulphur. Though it generally occurs in small nodules and granules, *nuggets* are sometimes found weighing many pounds. It is usually separated from the matrix by grinding and washing, or by amalgamation with mercury.

Gold may be obtained pure by dissolving standard gold in nitro-hydrochloric acid, evaporating the solution to dryness (by a gentle heat towards the end of the process), redissolving the dry mass in distilled water, filtering, acidulating by hydrochloric acid, and adding a solution of protosulphate of iron. A brown powder falls, which, after having been washed with hydrochloric acid and distilled water, affords, on fusion with a little borax or other suitable flux, a button of pure gold; ($6(FeO,SO_3)+AuCl_3=2(Fe_2O_3,3SO_3)+Fe_2Cl_3+Au$). If the solution from which the gold is precipitated is extremely dilute, it acquires on the first addition of the salt of iron a beautiful blue tint, when viewed by transmitted light, and appears reddish by reflection.

Gold is of a deep and peculiar yellow color. It melts at a bright-red heat, equivalent to about 2016° of Fahrenheit's scale, and when in fusion appears of a greenish color; as it solidifies it contracts in bulk. Its specific gravity, in its least dense state, after fusion, is 19·2; by hammering and rolling it may be brought up to 19·3 or 19·4. It is so malleable, that it may be beaten into leaves which do not exceed the 1-200,000th of an inch in thickness; a single grain may be extended over 56 square inches of surface; and it is so ductile that a grain may be drawn out into 500 feet of wire. It may be kept for several hours in fusion without perceptible loss of weight; but when subjected to an intense heat it affords evidence of volatility. The concentrated mineral acids have separately no action upon pure gold; neither has sulphur nor sulphuretted hydrogen. Chlorine, iodine, and bromine, on the contrary, are capable of acting upon it; the agent commonly resorted to for dissolving it, is chlorine, generally in the form of nitrohydrochloric acid, or *aqua regia.* If a small portion of leaf-gold is added to a freshly-made solution of chlorine, and the mixture is heated, the gold is speedily dissolved, forming a yellow-colored liquid. Any silver that may be present, will remain in dark-colored particles undissolved. Bromine water also dissolves gold. When gold is boiled with hydrochloric acid, and a small quantity either of peroxide of manganese, or of an alkaline seleniate is added to the liquid, the metal is immediately dissolved. Chlorine is set free in both cases (pp. 173 and 216).

There are two oxides of gold, a *protoxide* and a *peroxide.*

PROTOXIDE OF GOLD; *Aurous Oxide* (AuO) is obtained by precipitating a solution of the protochloride by a weak solution of potassa. It is of a dark color, and is converted by hydrochloric acid into metallic gold and perchloride; potassa and soda dissolve a little of it; with ammonia it forms a detonating compound.

PEROXIDE OF GOLD. *Auric Oxide; Auric Acid* (AuO_3).—The best process for obtaining peroxide of gold consists in the decomposition of the *perchloride* by magnesia, washing the precipitate with dilute nitric acid, and drying it at a low heat. It is of a brown color, and is reduced by the action of light, or when heated to 480°. It dissolves in sulphuric and in nitric acids, but the solutions are decomposed by dilution with water. It is soluble in the hydracids, and combines, when hydrated, with alkaline bases, forming salts which have been called *Aurates.* With ammonia it forms a fulminating compound.

PROTOCHLORIDE OF GOLD ($AuCl$) is obtained by exposing the perchloride to a temperature not exceeding 350°: it loses chlorine, and is converted into a pale-yellow *protochloride,* which is very unstable, and is decomposed by the action of boiling water.

PERCHLORIDE OF GOLD ($AuCl_3$).—The common solvent of gold, for the purpose of obtaining the chloride, is the nitrohydrochloric acid. Six grains of pure gold (dentist's foil) may be dissolved in ½ a drachm of pure nitric and 1½ drachms of pure hydrochloric acid. A gentle heat should be employed, and the acid liquid concentrated by evaporation on a sand-bath, until it is reduced to one-third of its bulk. It may then be set aside for crystallization, or at once mixed with a quantity of water, in proportion to the strength of solution required. The chemical changes may be thus represented: ($Au+NO_5+3HCl=AuCl_3+3HO+NO_2$). By evaporating a saturated solution, prismatic crystals of a deep orange-color are obtained. These are very deliquescent, fusible, and decomposed by heat, yielding, at first the protochloride, and ultimately, pure gold. The solution, even when much diluted, has a rich yellow color. It is decomposed by phosphorus, charcoal, sulphurous and gallic acids, and many of the metals and their compounds. A piece of paper or gelatin moistened with it and exposed to light, becomes purple from the separation of metallic gold. When heated with oxalic acid, carbonic acid gas is evolved, and gold is precipitated. Protosulphate of iron throws down the metal in a finely-divided state, and in this condition it is used for gilding porcelain, and other purposes (p. 480).

Perchloride of gold dissolves in alcohol and in ether: the latter solution is obtained by agitating the aqueous solution of gold with ether, after which the mixture separates into two portions; the superior is yellow, and is an ethereal solution of chloride of gold; the inferior is colorless, being water and hydrochloric acid. Polished steel dipped into this ethereal solution acquires a coating of gold, and it has hence been employed for gilding delicate cutting instruments. When long kept, it often slowly deposits films of metallic gold, in arborescent crystals.

PURPLE OF CASSIUS.—When a dilute mixed solution of protochloride and perchloride of tin is gradually added to a dilute solution of perchloride of gold, this purple compound is precipitated; and if a piece of tinfoil be immersed in a dilute solution of the chloride, the same purple powder is thrown down.

The purple of Cassius is used in enamel and porcelain painting, and also for tinging glass of a fine red. It retains its color at a high red heat: it is insoluble in solutions of potassa and soda; but if, whilst in its hydrated state, it is washed with ammonia, a bright purple liquid is obtained. This compound is regarded as a hydrated stannate of gold and tin (AuO,SnO_2+SnO,SnO_2+4Aq).

AURO-PERCHLORIDES.—These are compounds in which the chloride of gold is combined with certain electro-positive chlorides, such as those of the alkaline bases: they consist of 1 atom of perchloride of gold, and 1 atom of the other chloride, and may be formed of their respective chlorides in such proportions. Some of them have been long known: they mostly form prismatic crystals, and include water of crystallization. It is in consequence of the formation of these soluble double salts, that a solution of perchloride of gold in hydrochloric acid, yields no precipitates with the alkalies, even when added in excess. Different aurochlorides, obtained by adding salts of potassa, soda, ammonia, and other bases, to the chloride, are employed in gilding copper trinkets, buttons, and other articles.

IODIDES and BROMIDES of gold, corresponding to the chlorides, have been formed. They also produce double salts with the *electropositive iodides and bromides.*

SULPHIDE OF GOLD (AuS,AuS_3) is produced by passing sulphuretted hydrogen through a cold and diluted aqueous solution of perchloride of gold. It falls in the form of a black powder, and is resolved by heat into gold and sulphur. It is soluble in alkaline sulphides. A double *sulphide of gold and potassium* is formed, when sulphide of gold is digested in a solution of sulphide of potassium; or when gold, sulphur, and potassa are fused together; the compound is soluble in water. Sulphide of gold is used in the Potteries as a source of the preparation of gold with which a dingy gilding is given to porcelain. When sulphuretted hydrogen is passed through a boiling solution of chloride of gold, the metal is precipitated: $4AuCl_3+3HS+9HO=4Au+12HCl+3SO_3$.

Protocyanide of Gold ($AuCy$) falls in the form of a yellow crystalline precipitate on adding a solution of cyanide of potassium to a dilute solution of perchloride of gold. Its most important compound is that with cyanide of potassium, which may be formed by dissolving either cyanide of gold, or the compound obtained by precipitating a solution of perchloride of gold by ammonia, in a solution of cyanide of potassium. Its concentrated solution gives crystals$=KCy,AuCy$. It is used for gilding silver and copper, and especially for electro-plating.

Percyanide of Gold ($AuCy_3$) is formed by mixing a solution of caustic potassa, to which excess of hydrocyanic acid has been added, with perchloride of gold free from uncombined acid. It yields crystals$=AuCy_3+6Aq$. It forms double salts with the cyanides of the alkaline bases.

Alloys of Gold.—The most important are those with copper, mercury, and silver. With *copper*, gold forms a ductile alloy of a deeper color, harder, and more fusible than pure gold: this alloy, in the proportion of 11 gold to 1 copper, or 91·67 gold, 8·33 copper, constitutes *standard gold;* its density is 17·157, being a little below the mean. One troy pound of this alloy is coined into $46\frac{29}{40}$ sovereigns, or 20 troy pounds into 934 sovereigns and a half. The pound was formerly coined into 44 guineas and a half. The standard gold of France consists of 9 parts of gold and 1 of copper. Standard gold is not affected by nitric acid; but the inferior alloys which are made to imitate gold, consisting chiefly of copper and zinc, immediately decompose this acid, and set free deutoxide of nitrogen. The insolubility of gold in strong nitric acid distinguishes it from these alloys. In testing small articles of jewelry the following plan may be adopted. The metal may be rubbed upon a smooth surface of blood-stone or jasper, so as to transfer a portion to the stone. One or two drops of strong nitric acid are then placed on the metallized surface of the stone. If the article is a base alloy, the metallic appearance is speedily destroyed, and the metal is dissolved: if gold, it remains unaffected. Base alloys are frequently plated with gold, and in this case the only method of judging of the quality of the metal, is by taking the specific gravity, which should be at least 17 for standard gold. Trinket-gold is seldom above 15; and the so-called gold chains ordinarily met with vary from 11 to 13. Common gilt articles vary from 7 to 9.

Mercury and gold combine readily, especially when heated, the mercury taking up a considerable proportion of gold without loss of fluidity: when rich in gold, the amalgam is of a buttery consistence, and may be separated from the more liquid portion by pressure through leather; it then consists of about two parts of gold and one of mercury: the amalgam used for gilding bronze contains about one-eighth of gold. *Silver* and gold mix readily in all proportions, when the fused metals are stirred together. The standard gold at present coined, is for the most part alloyed with copper only; previous to the year 1826, the alloy consisted in part of silver, hence its paler color. To separate the silver from gold, the alloy is melted with a great excess of silver, granulated, and boiled in sulphuric acid, by which the silver is oxidized and converted into sulphate, and the metallic gold remains in the form of a dark insoluble powder, which is afterwards collected, washed, and fused into a button or ingot. In the same way, the small quantity of gold contained in silver coin, which used to pass unheeded, is extracted by sulphuric acid; the recently coined silver will accordingly be found, in most cases, destitute of those traces of gold which are contained in our coin of a date anterior to 1826. When gold and silver are parted by the action of nitric acid, it is necessary, as in the case of sulphuric acid, that the silver should be in great excess; it is otherwise protected from the solvent power of the acid.

Assay of Gold.—The quantity of standard or other gold used for assay is generally about 8 grains: to this, about three times its weight of pure silver, together with the proper proportion of lead is added, and the whole subjected to *cupellation*, as already described (page 467). The silver and gold are thus thoroughly combined, while the oxides of lead and copper are absorbed by the cupel. The auriferous button is then flattened under the hammer, and after having been annealed, is passed between a pair of small rollers, so as to extend it into a thin ribbon: it is then again annealed, and coiled up so as to form what is called a *cornet*, which is put into a flask or matrass containing about an ounce of hot nitric acid, sp. gr. 1·180, and boiled for about ten minutes, by which the silver is dissolved, and the gold, retaining the form of the cornet, remains: this is again boiled for about twenty minutes in somewhat stronger nitric acid, and then carefully washed and transferred to a small crucible, in which it is heated to redness. When cold, the loss upon the original weight of the sample, is carefully ascertained. The weight of the alloy operated upon is always represented as=1000, and the weights used are so adjusted as to give the value of the alloy in thousandths. In the process of gold-assaying, as in that of silver, various errors have to be compensated for, more especially in reference to the traces of copper, lead, and silver which may have been left in the gold.

Tests for the Salts of Gold.—Such of these as are soluble are distinguished by the peculiar purple precipitates which they afford with the mixed chlorides of tin. Protosulphate of iron, and oxalic and sulphurous acids throw down metallic gold. They are all decomposed by heat, and the residuary gold is easily recognized.

Platinum (Pt=99).

This metal was first made known in 1741. Its name is derived from *platina*, a diminutive of the Spanish word *plata*, silver.

Platinum is found in the metallic state, in small grains, confined to streams and alluvial strata, chiefly in Brazil and Peru, and in the Uralian mountains of Siberia. The grains, besides platinum, contain generally gold, iron, lead, palladium, rhodium, iridium, and osmium, and often oxide of titanium and chromate of iron. Rounded masses of the metal occasionally occur among them; these are rarely larger than a pea or a small marble, though some have been found of the size of a pigeon's egg. The usual mode of obtaining pure platinum consists in digesting the ore in nitrohydrochloric acid, decanting the clear solution from the black insoluble residue, and mixing it with a solution of sal-ammoniac; a yellow double chloride of ammonium and platinum falls ($NH_4Cl,PtCl_2$), which, when well washed and heated to redness, leaves a spongy mass of finely-divided metal; this is triturated with water, and subjected to powerful pressure in a brass mould, so as to form a porous ingot, which is gradually raised to a white heat and carefully hammered at its ends, until it forms a coherent bar.

Malleable platinum has lately been manufactured by the following process, contrived by Deville and Debray. The prepared ore is fused with its weight of sulphide of lead and half its weight of metallic lead; some of the impurities are thus separated in combination with sulphur, while the platinum forms an alloy with the lead, which is freed from the scoriæ, and subjected to the joint action of heat and air, until the greater part of the lead is oxidized into litharge, so that the residuary alloy only retains about 5 per cent. of lead. It is then subjected to the intense heat of an oxyhydrogen flame in a furnace of chalklime, where the rest of the lead (together with any gold, copper, and osmium) is driven off in fumes: the remaining platinum is cast into any required form. This process, which has furnished ingots of more than 50 pounds in weight, leaves some rhodium and iridium in combination with the platinum; but these metals do not affect its useful applications, neither rendering it more fusible nor more liable to the action of acids.

In the International Exhibition of 1862, Messrs. Johnson exhibited a mass of pure platinum, prepared by Deville's process, weighing 230 pounds, and valued at 3840*l.* In the production of this enormous mass of a metal hitherto regarded as infusible, the operator was nearly killed by the fumes of osmic acid evolved.

The color of platinum is between that of iron and silver. When pure it scarcely yields in malleability to gold and silver: it is excessively ductile and tenacious, and takes a good polish: it is harder than copper, but softer than iron. The specific gravity of platinum fluctuates between 21 and 22. Its extreme difficulty of fusion, and the perfect manner in which it resists the action of almost all acids, at a boiling or even at a red heat, render it importantly useful in many of the arts, and indispensable in the laboratory. The curious catalytic action of clean surfaces of platinum, of pulverulent and spongy platinum, and platinum black, upon gaseous mixtures, especially in determining the combination of oxygen and hydrogen, has rendered this metal useful in gaseous analyses. Bibulous paper, or fibres of asbestos, saturated with a strong solution of chloride of platinum, dried, and ignited, yield an ash which exhibits the properties of finely-divided platinum in perfection. This *catalytic* action of platinum appears increased in proportion to the mechanical division of the metal and the perfect cleanliness of its surface.

Catalytic platinum may be prepared by dissolving protochloride of platinum in a strong hot solution of caustic potassa, and adding alcohol: the hot mixture is stirred till the effervescence, arising from the escape of carbonic acid ceases; this is so violent as to require the use of a capacious vessel. The platinum falls in the form of a black powder, from which the supernatant liquor is poured off; the powder is then boiled successively in alcohol, in hydrochloric acid, and in solution of potassa, and lastly, in four or five portions of distilled water. If the alcohol is not entirely removed the powder ignites on drying, and loses its catalytic power. It is dissolved by a solution of chlorine. When dry, it looks like lamp-black, but acquires a metallic aspect after having been heated white-hot. This form of platinum is also obtained by heating an aqueous solution of 4 parts of bichloride of platinum, 10 of crystallized carbonate of soda, and 1 of grape-sugar to 212°, stirring the liquor till the whole of the black precipitate has fallen, which is then well washed and dried: it is improved by boiling it first in nitric acid, and then in solution of potassa, and finally washing and drying.

Catalytic platinum absorbs gases, which, without combining with it, become condensed in its pores. Exposed to air, it absorbs oxygen to the extent of 250 times its volume. It induces various combinations: its action on mixtures of oxygen and hydrogen has already been noticed (pp. 54, 117).

Although pure platinum is infusible in an ordinary wind furnace, it softens so as to admit of welding and forging. In the arc of flame of the voltaic current, and before the oxyhydrogen blowpipe, in a lime-furnace, it not only admits of being fused, but when very intensely heated it is said to give off vapor.

Although pure platinum is insoluble in nitric acid, yet when alloyed with certain other metals soluble in this acid, it is taken up; as for instance, with silver. It is attacked at high temperatures by the alkalies, especially by baryta, lithia, and potassa, and also by nitre and the alkaline persulphides: it is not affected by sulphur unless in the spongy state, but it combines with the greater number of the metals, and with many of them forms very fusible compounds; these actions show the necessity of caution as to the substances which are ignited or fused in platinum crucibles, and as to the fuel with which they are brought into contact.

The affinity of platinum for oxygen is, like that of gold, extremely feeble; it shows no disposition to become an oxide by exposure to air or oxygen at any temperature; and although a strong electric discharge, when transmitted through a fine platinum wire, dissipates it into black dust, this, as in the analogous case of gold, is probably finely-divided metal, and not the result of oxidation. Two oxides of platinum have been satisfactorily identified.

PROTOXIDE OF PLATINUM (PtO).—When protochloride of platinum is gently heated in a solution of caustic potassa, a black oxide is formed, part of which is dissolved, and part precipitated: it may be thrown down from its alkaline solution by dilute sulphuric acid. It is easily reduced by heat, and slowly dissolves in the acids, most of which decompose it, and resolve it into peroxide and metal.

BINOXIDE OF PLATINUM; PEROXIDE OF PLATINUM (PtO_2) is obtained by decomposing nitrate of platinum by carbonate of soda, so as to leave the nitrate in excess. It falls in the form of a brown hydrate, which, when heated, first gives out water and becomes black; at a higher temperature it evolves oxygen, and is reduced: it has a feeble attraction for the acids, but combines with many salifiable bases, and dissolves in the caustic and carbonated alkalies. It forms a fulminating ammoniacal compound, similar to fulminating gold.

PROTOCHLORIDE OF PLATINUM ($PtCl$).—When perchloride of platinum is exposed in a porcelain capsule to a temperature not exceeding that of melting tin (about 400°), and stirred so long as it evolves chlorine, it is converted into a gray powder, insoluble in water, and not decomposed by sulphuric or nitric acid, but soluble in boiling hydrochloric acid. It forms crystallizable double salts with the alkaline chlorides. It is decomposed at a red heat.

BICHLORIDE OF PLATINUM; PERCHLORIDE OF PLATINUM ($PtCl_2$).—When a solution of platinum in nitrohydrochloric acid is evaporated, it affords a deep-brown liquid which shoots into prismatic crystals, consisting of hydrated perchloride of platinum and hydrochloric acid; on further evaporation it yields a brown saline mass, which becomes deeper colored upon the expulsion of its combined water. It is then a *perchloride of platinum*, yielding a deep yellow solution in water, and soluble in alcohol and in ether. It combines with many other chlorides, forming an extensive class of double salts.

The AMMONIO-BICHLORIDE OF PLATINUM ($NH_4Cl+PtCl_2$) is the yellow powder which falls when solutions of bichloride of platinum and sal-ammoniac are mixed. When exposed to heat, it loses a little water, and at a red heat it evolves nitrogen, hydrochloric acid, and sal-ammoniac, without undergoing fusion, and the platinum remains in the peculiar spongy state before referred to. This ammonio-chloride is sparingly soluble in pure water; it is insoluble in cold hydrochloric acid, and falls as a crystalline powder from its solution in hot hydrochloric acid. It is almost entirely insoluble in solution of sal-ammoniac, and it is insoluble in alcohol.

The *action of ammonia* on the two chlorides of platinum gives rise to a series of *compound bases* which have much theoretical, but little practical interest, and which have hitherto been only imperfectly examined as to properties and preparation. Any condensed notice of these, compatible with the limits of this work, would be useless to the student.

POTASSIO-BICHLORIDE OF PLATINUM ($KCl,PtCl_2$) is thrown down in the form of a yellow powder, when concentrated solutions of chloride of potassium and of bichloride of platinum are mixed: it is very sparingly soluble in water, and is deposited from its boiling solution in small octahedral crystals. It is insoluble in alcohol. The difficult solubility of this compound renders bichloride of platinum a useful test of the presence of the salts of potassa, as well as of the salts of rubidium and cæsium. The platino-chlorides of these two metals, however, are much less soluble than the platino-chlorides of potassium: hence a solution of the latter gives a dense yellow precipitate in a salt of cæsium or rubidium.

SODIO-BICHLORIDE OF PLATINUM ($NaCl,PtCl_2$).—Chloride of sodium occasions no precipitate with bichloride of platinum, but the mixed solutions yield on evaporation prismatic crystals, of a deep orange color, soluble in water and in alcohol, and which, when heated, lose 6 atoms of water of crystallization, leaving the anhydrous double salt. A variety of other analogous double salts have been described; they are generally made by mixing the two chlorides in atomic proportions.

The *Bibromide* and *Biniodide* of platinum are sparingly soluble in water, and are obtained by the decomposition of the bichloride, by bromide and iodide of potassium.

PROTOSULPHIDE OF PLATINUM (PtS) may be formed by heating finely-divided platinum with sulphur, or by the decomposition of protochloride of platinum by sulphuretted hydrogen. It is a gray or black powder, unaltered by air or water, scarcely attacked by the boiling acids, but decomposed when heated in the air.

BISULPHIDE OF PLATINUM (PtS_2) falls in the form of a brownish powder, when the sodio-bichloride of platinum is precipitated by sulphuretted hydrogen: at a red heat it is decomposed, and leaves metallic platinum.

PROTOSULPHATE OF PLATINUM (PtO,SO_3) is obtained when a solution of protoxide of platinum in caustic potassa is saturated with sulphuric acid, the liquid poured off, and the precipitate dissolved in dilute sulphuric acid: the concentrated solution is black; diluted with water it becomes red, and passes into persulphate.

PERSULPHATE OF PLATINUM ($PtO_2,2SO_3$) is obtained by acidifying the sulphur of the sulphides of platinum by nitric acid. It is deep brown, and soluble in water, alcohol, and ether: with soda, potassa, and ammonia, it forms double salts.

CYANIDE OF PLATINUM forms a series of *double cyanides*, some of which are extremely beautiful. The *platino-cyanide of potassium* ($KCy,PtCy$) or ($K,PtCy_2$) formed by dissolving protochloride of platinum in a solution of cyanide of potassium, forms prismatic crystals, yellow by transmitted, and blue by reflected light. They contain 3 atoms of water. The *platino-cyanide of magnesium* forms crystals which exhibit various shades of red, blue, and green (p. 32).

When chlorine is passed through a solution of the platino-cyanide of potassium, crystals are deposited which are green by transmitted light, but of a copper color by reflected light. This salt, termed *sesquiplatino-cyanide of potassium*, has the formula ($K_2,Pt_2Cy_3,6Aq$).

ALLOYS OF PLATINUM.—*Iron* and platinum in equal parts form a crystalline alloy, which takes a fine polish. Platinum dissolves in fused *zinc;* the alloy is bluish-white, brittle, and hard. Zinc heated in platinum-foil before the blowpipe burns vividly and even with explosion. *Tin* and platinum form alloys more or less brittle and fusible. When tin-foil and platinum are wrapped together and heated by the blowpipe, they combine with incandescence. With its weight of *nickel* platinum forms a pale yellow alloy, susceptible of a high polish. *Copper* and platinum form alloys, the ductility and color of which vary with the proportions: platinum easily destroys the color of copper: an alloy of 7 platinum, 16 copper, 1 zinc, resembles gold in color. *Lead* and platinum form brittle alloys. Platinum and lead-foil folded together and heated before the blowpipe, combine with elevation of temperature. *Antimony* and platinum readily enter into ignition when they combine, in the same manner as tin and zinc. *Arsenic* and platinum form a dark-gray brittle alloy. When particles of arsenic are placed upon red hot platinum-leaf, they immediately fuse a hole in it. *Mercury* amalgamates difficultly with platinum: spongy platinum forms the readiest combination, especially when rubbed with the mercury in a hot mortar. *Silver* and platinum form ductile alloys. *Gold* and platinum require a strong heat for combination, and the color of the gold is greatly deteriorated.

The perfection with which vessels of platinum resist the action of heat, and of most acids, renders them peculiarly valuable in many of their applications; but its high price is against its general adoption. In the employment of platinum-vessels, the following precautions must be attended to: 1. They must not be subjected to the action of compounds which evolve chlorine. 2. Nitre, and the alkalies, must not be fused in them. 3. No metallic reductions must be performed in them; nor compounds of phosphorus decomposed, so as to evolve that substance. 4. When metallic oxides are heated in a platinum crucible, the heat must not be raised to redness, provided the oxide is easily decomposed. 5. The immediate contact of the fuel (charcoal should always be used) with the crucible should be avoided, especially at very high temperatures; for it is thus rendered brittle and unsound.

TEST FOR THE SALTS OF PLATINUM.—The color and the difficult solubility of the ammonio and potassio-chlorides of platinum, and the solubility of the corresponding soda-compound, are very characteristic of this metal. All the metals which reduce the chloride of gold, with the exception of palladium, act similarly upon chloride of platinum, but its complete separation in the metallic state is slow: iron, zinc, cadmium, and copper, are its most effective precipitants; they separate it as a black powder, which sometimes adheres in films to the glass. Protosulphate of iron and tincture of galls occasion no precipitates in a solution of perchloride of platinum, a circumstance which distinguishes this metal from gold, silver, and palladium.

CHAPTER XLI.

PALLADIUM. RHODIUM. RUTHENIUM. OSMIUM. IRIDIUM.

PALLADIUM (Pd=54).

PALLADIUM was discovered by Wollaston in 1803: it is associated with the other metals mentioned in the last section as constituting the ore of platinum. It has also been found alloyed with gold.

Palladium is separated from the ore of platinum by the following process. Digest the *ore* in nitrohydrochloric acid, neutralize the redundant acid by soda, throw down the platinum by sal-ammoniac, and filter: to the filtered liquor add a solution of cyanide of mercury: a yellow flocculent precipitate of *cyanide of palladium* is soon deposited, which yields palladium on exposure to heat.

Palladium has a dull-white color, is malleable and ductile, but hard. It fuses at a temperature above that required for the fusion of gold, and when intensely heated by the oxyhydrogen blowpipe, it is dissipated in sparks. When heated over the flame of a spirit-lamp, it acquires various shades of blue upon its surface, in consequence of superficial oxidation. It is acted on by the greater number of the acids when aided by heat, and also by potassa and nitre: it has a strong affinity for cyanogen.

PROTOXIDE OF PALLADIUM (PdO).—When nitrate of palladium is precipitated by an alkali, the red or dark-orange powder which falls, is a *hydrated oxide.* In this state, it is soluble in acids, yielding red and brown salts of an astringent taste. It becomes black and anhydrous at a dull red heat.

BINOXIDE OF PALLADIUM (PdO_2) is obtained as a brown hydrate, by the action of a solution of potassa on the potassio-chloride of palladium.

PROTOCHLORIDE OF PALLADIUM ($PdCl$) is obtained by digesting palladium in hydrochloric acid with a little nitric acid, and evaporating to dryness: it forms a brown powder, which is nearly black when anhydrous. It forms double salts with the basic metallic chlorides, which are soluble in water and in alcohol. With ammonia it forms a series of compounds resembling those of platinum.

BICHLORIDE OF PALLADIUM; PERCHLORIDE OF PALLADIUM ($PdCl_2$) is only known in solution. It forms red double salts with the alkaline chlorides.

NITRATE OF PALLADIUM.—Palladium, when aided by heat, dissolves slowly in nitric acid, forming a brown solution which leaves a brown subnitrate on evaporation. Nitrate of protoxide of palladium forms a double salt with ammonia.

SULPHIDE OF PALLADIUM (PdS) is formed by fusing sulphur with palladium; it is white, hard, and fusible, and when long exposed to heat and air, it loses its sulphur. It is thrown down in the form of a black powder by the action of sulphuretted hydrogen upon the salts of palladium.

PROTOSULPHATE OF PALLADIUM (PdO,SO_3) is obtained by boiling the protonitrate to dryness with sulphuric acid; or by boiling the metal in sulphuric acid, when sulphurous acid is evolved, and a brown solution is obtained, which deposits the sulphate in red crystals. This salt, dissolved in aqueous ammonia, yields two *ammonio-sulphates* $=NH_3,PdO,SO_3$ and $2(NH_3)PdO,SO_3$.

CARBIDE OF PALLADIUM.—Palladium acquires brittleness when fused in contact with charcoal. When a plate of palladium is long held in the flame of alcohol, carbonaceous excrescences gradually form upon it, which, when burned, leave palladium. This property of precipitating charcoal from flame, and combining with it, is peculiar to palladium; platinum and iron only show slight indications of it.

CYANIDE OF PALLADIUM ($PdCy$) is formed when a solution of cyanide of mercury is added to a neutral solution of palladium: it falls in olive-colored or dingy yellow flakes; this furnishes a method of separating palladium from other metals which are incapable of decomposing the cyanide of mercury. It dissolves in cyanide of potassium, and forms *palladio-cyanide of potassium.* There is also a corresponding ammoniacal salt.

TESTS FOR THE SALTS OF PALLADIUM.—The fixed alkalies throw down red or orange precipitates from the solutions of palladium, sparingly soluble in excess of the alkali. Ferrocyanide of potassium gives an olive-green precipitate; and sulphuretted hydrogen one of a dark-brown color. Protochloride of tin occasions a brown precipitate in the neutralized solutions of palladium; when dilute, the mixture becomes green. Protosulphate of iron throws down metallic palladium. Cyanide of mercury forms a precipitate in all the salts of palladium, when the acid is not in excess. Iodide of potassium occasions a black precipitate of iodide of palladium in very dilute solutions. Chloride of palladium added to a solution of 1 part of iodide of potassium in 400,000 of water produces a brown tint.

RHODIUM (R=52).

After the platinum and palladium have been separated from the nitrohydrochloric solution of the crude ore, by sal-ammoniac and cyanide of mercury, and any excess of the cyanide has been decomposed by the addition of hydrochloric acid, chloride of sodium is added, and the liquor evaporated to dryness; the residue is then digested in alcohol, which leaves a red insoluble double chloride of sodium and rhodium. When this is dissolved in water, and a plate of zinc immersed, metallic rhodium is thrown down; or the double chloride may be at once decomposed by heating it in a current of hydrogen.

Rhodium, discovered by Wollaston in 1808, is a white metal very difficult of fusion, and extremely hard and brittle. When pure, the acids do not dissolve it, but they act upon several of its alloys. It may be oxidized by ignition either with nitre or with bisulphate of potassa, and, when heated with the latter, a double sulphate of peroxide of rhodium and potassa is produced. It may be oxidized by the joint action of heat and air, but the protoxide=RO, has not been examined in an isolated state. The salifiable oxide is R_2O_3.

SESQUIOXIDE OF RHODIUM (R_2O_3).—This oxide is obtained by heating finely-divided rhodium with caustic potassa and a little nitre to redness in a silver crucible, washing the product, and digesting it in hydrochloric acid: a greenish-gray hydrated oxide remains, which is insoluble in acids.

PROTOCHLORIDE OF RHODIUM (RCl) is obtained by passing dry chlorine over heated protosulphide of rhodium: it is reduced when heated in hydrogen.

SESQUICHLORIDE OF RHODIUM (R_2Cl_3) is obtained by adding fluosilicic acid to an aqueous solution of rhodiochloride of potassium, filtering, evaporating, dissolving the residue in water, and evaporating again with the addition of hydrochloric acid. This is a dark-brown compound, which deliquesces on exposure to air, and forms a red solution with water, and with alcohol. This chloride combines with many other chlorides to form double salts (*Rhodiochlorides*), which are of a red color: hence the name of the metal.

RHODIOCHLORIDE OF AMMONIUM; AMMONIO-SESQUICHLORIDE OF RHODIUM ($2(NH_4Cl)R_2Cl_3$), is obtained by evaporating a mixed solution of chloride of rhodium and sal-ammoniac: it forms brilliant garnet-colored prisms, which, when decomposed by heat, leave 31 per cent. of rhodium.

PROTOSULPHIDE OF RHODIUM (RS) is obtained by heating the ammoniochloride with sulphur: when heated in the air it leaves spongy rhodium.

SESQUISULPHIDE OF RHODIUM (R_2S_3) is thrown down in the form of a brown hydrate, by adding hydrosulphate of ammonia to a hot solution of rhodiochloride of sodium.

CHARACTERS OF THE SALTS OF RHODIUM.—The salts of the sesquioxide are mostly red; they are reducible by hydrogen and by zinc; sulphuretted hydrogen occasions a brown, and ammonia a yellow, precipitate in them. A hydrated oxide of rhodium, of a red-brown color, is thrown down by lime-water from a solution of the sesquichloride of rhodium in hydrochloric acid.

RUTHENIUM (Ru=52).

This is one of the metals remaining in that portion of the ore of platinum which resists the reaction of aqua regia: it has been imperfectly examined, but is stated to be hard, brittle, infusible in the oxyhydrogen flame, but readily oxidized by fusion with nitre, and furnishing four oxides. Of these, the peroxide, or *Ruthenic acid* (RuO_3), is produced when the other oxides are heated with nitre. The sesquioxide (Ru_2O_3) is obtained by heating the metal in the air: it forms soluble yellow salts with the acids, from which the alkalies throw it down in the form of a brown hydrate.

When a solution of sesquichloride of ruthenium is decomposed by sulphuretted hydrogen, a brown sulphide falls, and the supernatant liquid retains a protochloride in solution, and is of a bright blue color: this is the most marked character of the metal.

OSMIUM (Os=100).

Osmium and iridium, discovered by Tennant in 1803, are also contained in the residue of the action of nitrohydrochloric acid upon the ore of platinum. This residue, when fused with potassa and washed, furnishes a yellow alkaline solution of oxide of osmium, which, when saturated by sulphuric acid and distilled, yields a colorless solution of this oxide, from which almost all the other metals throw down metallic osmium.

Obtained by precipitation, osmium is in the form of a black powder, which acquires a metallic lustre by friction. In its densest state, the sp. gr. of this metal appears to equal, or even slightly exceed, that of platinum.

When heated in the air osmium burns into an oxide, and exhales poisonous fumes having a peculiar odor, somewhat like that of chlorine; hence the name of the metal (from ὀσμή, *odor*), and most of its compounds may be recognized by exhaling this odor when heated with a little carbonate of soda before the blowpipe. It forms five oxides.

PROTOXIDE OF OSMIUM (OsO) is obtained by the action of pure alkalies on the protochloride: it falls in the forms of a nearly black *hydrate*, obstinately retaining a portion of alkali; it dissolves slowly in the acids, forming deep-green or greenish-brown solutions.

SESQUIOXIDE OF OSMIUM (Os_2O_3) has not been isolated, but is produced when the peroxide is heated with excess of ammonia.

BINOXIDE OF OSMIUM (OsO_2).—When a solution of bichloride of osmium is heated with carbonate of soda, the binoxide falls in the form of a dark gray powder.

TEROXIDE OF OSMIUM (OsO_3) is assumed to exist in certain salts of this metal, but it has not been isolated. It has the properties of a weak acid.

PEROXIDE OF OSMIUM; OSMIC ACID (OsO_4) is the volatile oxide above adverted to, and is obtained by the combustion of the metal in oxygen, by the action of boiling nitric acid, or by the fusion of osmium with nitre or with potassa. When osmium is heated, and a current of oxygen passed over it, yellowish crystals of the anhydrous peroxide are formed: these dissolve slowly in water, and readily in alcohol and ether; the solutions stain the skin black, and gradually deposit metallic osmium. It is reduced by sulphuretted hydrogen, and sulphide of osmium is formed. It has no acid reaction, but it combines with alkalies, and forms compounds which are permanent at high temperatures. When infusion of galls is dropped into its aqueous solution, a characteristic blue color is produced.

CHLORIDES OF OSMIUM.—Four chlorides of this metal have been described. When chlorine is transmitted over heated osmium, a dark green sublimate of *protochloride of osmium* is the result. This is succeeded by a red sublimate, which is the *bichloride*. The *sesquichloride* and *perchloride* have not been obtained in a separate state, but form double salts with chloride of potassium.

SULPHIDES OF OSMIUM.—Sulphur and osmium apparently combine in several proportions, for sulphuretted hydrogen precipitates it from all its solutions.

The remaining compounds of this remarkable metal have not been minutely examined, but the characters of its salts will be sufficiently obvious from the preceding statements.

IRIDIUM (Ir=99).

The alloy of Iridium and Osmium remaining after the ore of platinum has been digested in aqua regia, may be decomposed by fusing it with chloride of sodium, and then passing chlorine over the mixture, in a tube heated to dull redness; the resulting product is then digested in boiling water, and the filtered solution concentrated, mixed with nitric acid, and distilled; osmic acid passes over, and *iridio-chloride of sodium* remains, which, by the addition of sal-ammoniac, yields a precipitate of *iridio-chloride of ammonium:* this double salt is decomposed by heat, and metallic iridium remains.

Iridium is a hard, white, brittle metal, extremely difficult of fusion. It is not acted upon by acids, but its alloy with platinum is soluble in aqua regia, and it is oxidized when fused with nitre. When in a very finely-divided state, it has properties resembling those of platinum black.

OXIDES OF IRIDIUM.—There are three oxides of this metal, the solutions of which are of various colors: hence the name *Iridium* (from *Iris*, the rainbow) applied to it. The *protoxide* is thrown down by the action of potassa on the protochloride, in the form of a black powder, nearly insoluble in acids, but yielding, with potassa, a blue or purple solution. The *sesquioxide* is formed by fusing iridium with nitre. In its hydrated state, it is soluble in hydrochloric acid, giving a blue solution, which becomes green, and brown when heated. The *binoxide* falls as a blue hydrate, when a solution of bichloride of iridium is boiled with potassa.

CHLORIDES OF IRIDIUM.—The *protochloride* is formed by heated iridium in chlorine: it is of a dark olive color, and forms double salts with the alkaline chlorides. The *sesquichloride*, formed by dissolving the sesquioxide in hydrochloric acid, also produces double salts. The *bichloride* also forms double salts with other chlorides, many of which resemble the corresponding platinum compounds. The *iridio-bichloride of ammonium* is remarkable for the intense brownish-red color of its solution: it is said to communicate a decided tint to 40,000 parts of water.

ALLOYS OF IRIDIUM.—The greater number of these alloys, when digested in nitric acid, leave iridium; but nitrohydrochloric acid dissolves them when the proportion of iridium is not considerable. *The native alloy of iridium and osmium* forms small crystals of much lustre, harder than steel, and as refractory as iridium.

In consequence of the difficult fusibility of iridium, and of the native alloy, grains of it are sometimes diffused through ingots of gold, and remain after a number of successive fusions. In coined gold moneys, it occasionally happens that one or more of these grains may be discerned; and where large quantities of gold are melted, they sink to the bottom of the crucible, so that in great gold coinages at the Mint, it has occasionally happened that several ounces of the ore of iridium have been thus accumulated.

There are some peculiarities belonging to the six preceding metals—namely, platinum and its associates—which deserve notice, in reference to their atomic weights and their specific gravities, and which have led to their division into two groups of three each, as follows :—

	Sp. gr.	Atom. Wt.		Sp. gr.	Atom. Wt.
Platinum . .	21.15	99	Palladium . .	11·8	54
Iridium . .	21·15	99	Rhodium . .	12·0	52
Osmium . .	21·40	100	Ruthenium . .	11·3	52

It will be observed that the specific gravities and atomic weights of the first group are almost identical; so also are those of the second group, the specific gravities and atomic weights of which are almost precisely one-half of those of the first group.

CHAPTER XLII.

QUALITATIVE ANALYSIS OF THE MOST IMPORTANT OF THE PRECEDING METALS.

In giving a summary of the methods of detecting the salts of the metals, not included in the 28th chapter, we propose making a selection of those which are more likely to fall in the way of a student. They may be represented by the following eighteen bodies: iron, manganese, zinc, tin, cadmium, lead, copper, bismuth, cobalt, nickel, chromium, uranium, antimony, arsenic, mercury, silver, gold, and platinum. They are here given in the order in which they have been treated in this volume. Referring in this place to the *solutions* of their salts, and to those compounds which are soluble, we may observe that many may be at once recognized by their peculiar colors, even when the liquids are much diluted. These are the salts of iron, manganese, copper, cobalt, nickel, chromium, uranium, gold and platinum.

The reagents which may be selected for the qualitative analysis of these metals are, sulphuretted hydrogen, hydrosulphate of ammonia, iodide of potassium, hydrochloric acid, ammonia, and ferrocyanide of potassium.

Among the *general* reagents employed in the analysis of metals, there is none so useful as *sulphuretted hydrogen.* The gas should be washed, and passed in a current into the suspected liquid, previously acidulated with hydrochloric acid. It produces in the liquid either a change of color or a colored precipitate (sulphide), which may be then easily identified by certain special characters.

The following metallic oxides are precipitated as sulphides from their solutions, of the colors mentioned below.

Yellow.	Orange red.
AsO_3 CdO	SbO_3
AsO_5 SnO_2	SbO_5

Arsenious acid is precipitated of a golden-yellow color, immediately; arsenic acid of a paler yellow color, slowly; oxide of cadmium is thrown down of a sulphur-yellow color; and peroxide of tin of a yellowish-brown color. The two arsenical sulphides are recognized by their entire solubility in ammonia, or in its hydrosulphate, as well as in a solution of potassa; and by their insolubility in strong hydrochloric acid. The sulphide of cadmium is insoluble in ammonia, potassa, and hydrosulphate of ammonia, but is dissolved readily by strong hydrochloric acid. The sulphide of tin is not soluble in ammonia, but is dissolved by the hydrosulphate, and by hydrochloric acid. The *hydrosulphate of ammonia* may be at once employed to divide the four oxides, which produce yellow sulphides, into two groups. For this purpose no hydrochloric acid should be added to the suspected liquids. The hydrosulphate produces no precipitate in solutions of arsenious and arsenic acids, but it precipitates at once the oxide of cadmium, and peroxide of tin. The sulphide of tin is distinguished from that of cadmium, not only by a striking difference of color, but by the fact that it is quite soluble in an excess of the hydrosulphate, while the sulphide of cadmium is insoluble in that liquid. The means of distinguishing arsenious from arsenic acid have been elsewhere fully explained (pages 443, 444). An *orange-red* precipitate is peculiar to antimony, whether the oxide is combined with a mineral or a vegetable acid. The precipitated sulphide is insoluble in ammonia. The antimonial compounds are similarly precipitated by hydrosulphate of ammonia, the orange-red sulphide being soluble in an excess of reagent.

The acid solutions of the following metals are precipitated or colored by a current of *sulphuretted hydrogen*:—

Precip. brown or black by Sulphuretted Hydrogen.		
$Hg\,O$	PbO	SnO
Hg_2O	CuO	AuO_3
$Ag\,O$	BiO_3	PtO_2

The persalts of mercury are thrown down at first of a yellowish color: the precipitate becomes black, only when the sulphuretted hydrogen has been passed into the liquid in large excess. Lead is not readily precipitated from very acid solutions; a solution of platinum is deepened in color by the gas, and only slowly precipitated.

Among the metallic oxides in this list, a salt of copper would be recognized by its blue color, a compound of gold by its rich yellow, and of platinum by its red-brown color. The application of ammonia, or the ferrocyanide of potassium, would serve to identify a cupreous salt. (*See* COPPER, page 394.) A solution of potassa would precipitate platinum, and not gold; while a solution of protosulphate of iron would precipitate gold (in a metallic state), and would not affect a solution of platinum.

The solutions of the remaining metallic oxides are colorless. One of these (bismuth) may be distinguished by the solution giving a white precipitate when added to distilled water. This precipitate is not dissolved by a solution of tartaric acid. (*See* BISMUTH, p. 407.)

The solutions of the other metals, much diluted, may be treated with a solution of *iodide of potassium:* they are then precipitated as iodides, of the following colors: Subsalts of mercury, yellow (insoluble in hydrochloric acid, and in potassa); persalts of mercury, scarlet (soluble in an excess of the reagent); salts of silver, pale yellow (insoluble in, but rendered white by ammonia); of lead, bright yellow (soluble in hydrochloric acid, and in potassa); the salts of protoxide of tin, pale yellow (soluble in hydrochloric acid, and potassa); the salts of bismuth produce a brown precipitate soluble in an excess of the iodide.

Although the solutions of copper, gold, and platinum, have been already excluded from the group, by color and their chemical properties, it may be desirable to place here the results produced by the addition of iodide of potassium to their diluted solutions. With a salt of copper, the iodide produces a yellow-brown precipitate of subiodide of copper; with gold, a yellow-green precipitate, iodine being set free; and with platinum, a deep wine-red colored liquid, which, on being heated, deposits platinum in a metallic state. The whole of the metals in this group are precipitated by *hydrosulphate of* *ammonia*, as brown or black sulphides. Of these, three only, the protoxide of tin, and the peroxides of gold and platinum, are dissolved by an excess of the reagent. The sulphide of tin requires a large excess for solution. *Hydrochloric acid* also serves as an eliminating test for the colorless metallic solutions of this group :—

$$\overbrace{Hg_2O\ AgO\ PbO}^{\text{Precipitated white.}} \qquad\qquad \overbrace{HgO\ BiO_3\ SnO}^{\text{Not precipitated.}}$$

The white precipitate given by lead, is soluble in boiling water: it is also dissolved with or without the aid of heat, by a solution of potassa, and by strong hydrochloric acid. The white precipitates, given by suboxide of mercury and oxide of silver, are insoluble in water, potassa, and in hydrochloric acid. The precipitated subchloride from suboxide of mercury is not soluble in ammonia, but is blackened by that alkali. The precipitated chloride of silver is quite soluble in ammonia, forming a colorless solution. Of the three not precipitated by the acid, a persalt of mercury is recognized by the black precipitate of metallic mercury given on the addition of a protosalt of tin; and a protosalt of tin by a similar precipitate being produced when a persalt of mercury is added to its solution. Bismuth may be recognized by the precipitate which it gives on the addition of water (p. 407.)

We have thus disposed of eleven metals of the selected group. The remaining seven are not precipitated by a current of *sulphuretted hydrogen*, in solutions acidulated with hydrochloric acid.

$$\overbrace{\begin{array}{lll} Fe\,O & NiO & MnO \\ Fe_2O_3 & CoO & U_2O_3 \\ Cr\,O_3 & ZnO & \end{array}}^{\text{Not precipitated by Sulphuretted Hydrogen.}}$$

When sulphuretted hydrogen is passed into a solution of peroxide of iron, the persalts are reduced to the state of protosalts, and there is a milky-white deposit of sulphur. In the salts of chromic acid, a green color is produced from the production of green oxide of chromium, which is dissolved in the acid liquid, and sulphur is separated.

Hydrosulphate of ammonia precipitates the whole of these metallic solutions :—

$$\overbrace{\begin{array}{ll} Fe\,O & CoO \\ Fe_2O_3 & U_2O_3 \\ Ni\,O & \end{array}}^{\text{P. black or brown.}} \qquad \overbrace{CrO_3}^{\text{Green.}} \qquad \overbrace{ZnO}^{\text{White.}} \qquad \overbrace{\quad MnO \quad}^{\text{Reddish-white.}}$$

Black sulphide of iron is produced by this test in salts of the protoxide and peroxide, a small quantity being suspended, and giving a greenish color to the liquid. When exposed to air, these precipitates are rapidly converted into reddish-brown hydrated peroxide of iron. In undergoing this rapid change by exposure to air, they are distinguished from the sulphides of nickel and cobalt. These precipitates are not soluble in an excess of the reagent. The other three metallic oxides are sufficiently characterized by the colors of their sulphides.

The *ferrocyanide* and *ferricyanide* of potassium may be here employed as useful eliminating reagents. The protosalts of iron are precipitated white or bluish-white by ferrocyanide, and deep blue by ferricyanide of potassium. The persalts are precipitated of a deep blue color by ferrocyanide, but not by ferricyanide of potassium; this liquid merely imparts to them a deep greenish tint. Ferrocyanide of potassium produces in the salts of nickel, a pale green precipitate, in the salts of cobalt, a dingy olive-green precipitate, and in the salts of peroxide of uranium, a deep red color or precipitate, resembling that produced in solutions of salts of copper. The cupreous precipitate is dissolved by ammonia with the production of a blue color, while the uranium precipitate is dissolved by this alkaline liquid, with the production of a pale yellow color. The action of this test upon the other members of this group, may be thus described. Oxide of zinc gives a white, and oxide of manganese a reddish-white precipitate. The presence of copper or iron, as an impurity, in these liquids, will of course affect the colors of the precipitates. A chromate is neither changed in color nor precipitated: a bichromate acquires a darker color.

Ferrocyanide of potassium is also useful as a *general* test. We subjoin a table of its reactions on the eighteen metals which have been here selected for qualitative analysis. The greater number of these metallic solutions are precipitated white, or of shades of white: some are not precipitated; while a few are thrown down of peculiar colors, by which they may in general be identified.

Not precipitated by ferrocyanide of potassium.

AsO_3	AsO_5	SbO_3	CrO_3	AuO_3	PtO_2
		With tartaric acid.		Emerald green color.	Pale green color.

Precipitated white by ferrocyanide of potassium.

SbO_3 SbO_5 AgO	$Hg\,O$ Hg_2O $Pb\,O$	BiO_3 SnO SnO_2	FeO ZnO CdO
Reddish-white.	Claret-red.	Blue.	Pale-green.
MnO.	CuO. U_2O_3.	F_2O_3.	NiO. CoO.

The oxides of antimony combined with organic acids, are not precipitated by this test.

The insoluble compounds of the metals may be brought into solution with hydrochloric or nitric acid; and the solutions, properly diluted, may then be submitted to the action of the tests here described.

The object of these rules is to point out the base, or oxide of the metal. When this has been indicated, the tests of a *special* kind, which are described under each metal, may then be applied.

THALLIUM.—Mr. Crookes has announced, as the result of spectrum-analysis, the existence of a new metal, which he has called *Thallium.* It is characterized by its vapor producing only one green line in the spectrum. He found it in certain kinds of sulphur, and has succeeded in obtaining it by electrolysis in a separate form. In its chemical and physical properties, if we except absence of lustre, it is said to bear a resemblance to lead; but it is heavier than this metal, and tarnishes more readily. Samples of this substance, the properties of which are yet under investigation, have been exhibited at a meeting of the Royal Society, and at the International Exhibition, 1862. (See *Chemical News*, July 5, 1862, p. 1.)

ORGANIC CHEMISTRY.

CHAPTER XLIII.

CONSTITUTION AND PROPERTIES OF ORGANIC SUBSTANCES. PROXIMATE ANALYSIS.

ORGANIC CHEMISTRY is that branch of the Science which refers to the properties and composition of organized products, or of substances which have been formed in vegetables and animals, under the influence of *life*. These products differ remarkably in physical and chemical characters from bodies which belong to the Mineral or Inorganic kingdom; and they may, in many cases, be at once distinguished by external appearance. In reference to chemical composition, they are also widely different. While they are constituted of a smaller number of elements, the atoms of each element are in general numerous, and are, at the same time, grouped in more complex forms, building up frequently intermediate compounds or proximate principles. The greater number of vegetable substances are constituted of only three elements, *Carbon*, *Hydrogen*, and *Oxygen*, of which carbon is the principal. Some organic substances contain only *two* elements, CH or CO, the compounds of HO being inorganic; but in these cases, the atoms of each are more numerous than in the mineral compounds of the same elements. One of the most simple in atomic constitution among organic substances, is probably anhydrous oxalic acid. It contains only two elements, and but a small number of atoms of each, being represented by the formula C_2O_3. In this simple state, however, it includes an atom of each of the inorganic compounds of the same elements, CO (carbonic oxide), and CO_2 (carbonic acid). The alkaloids, or vegetable alkalies, are at the other end of the scale. The most complex contain four elements, of which nitrogen is one; and with the exception of this, the atoms of each element are very numerous. Thus morphia, one of the alkaloids of opium, is represented by the following complex formula: $C_{35}H_{20}O_6N$, and its equivalent or combining weight is 292. The low saturating power of these organic bases, will account for the high numbers by which they are represented. Thus, 292 parts of morphia are only equivalent to 47 of potassa, 31 of soda, and 17 of ammonia. Other bodies, such as the neutral vegetable organic principles, gum, starch, and sugar, occupy an intermediate position. They consist of three elements, carbon, hydrogen, and oxygen, of which the oxygen and hydrogen are in the proportions to form water. Thus, cane-sugar and gum are $C_{12}H_{11}O_{11}$, and starch, dextrine, and cellulose are $C_{12}H_{10}O_{10}$, the differences among these bodies consisting chiefly in the presence or absence of one or more atoms of water. This curious relationship of the oxygen to the hydrogen in these bodies, long since attracted the notice of chemists, and it entered into one of the early systems of classification. It is not, however, peculiar to neutral substances, but is found occasionally among vegetable acids. Thus anhydrous acetic acid is $C_4H_3O_3$, and pyrogallic acid is $C_{12}H_6O_6$. It is a mere accident of constitution to which no importance can be attached, inasmuch as there is no reason to suppose that these elements are combined as water; and it is quite certain that the neutral properties of a compound do not depend upon any uniformity in the proportions of oxygen and hydrogen.

Isomeric Conditions.—The fact that two substances so different in physical and chemical properties as gum and sugar, are represented by the same number of atoms of the three elements, C,H,O, at once points to a peculiar character among organic products—namely, the frequent occurrence of *isomerism* among them. The meaning of this term has elsewhere been fully explained (p. 19); and illustrations of its two principal modifications, polymerism and metamerism, have been given. The word merely expresses the fact of a similarity of atomic proportions among different bodies; and the reasonable inference from the existence of this condition is, that the properties of organic compounds are referable to a different arrangement of their atoms, and not to their relative proportions. The atoms of carbon, oxygen, and hydrogen in gum are so numerous, that they admit of being arranged in a variety of groups; and, according to the order of grouping, so may the properties vary. Analysis might, therefore, show that two substances were identical in composition, while they were at the same time entirely different in properties. We agree with the observation of Pelouze and Fremy, that in the present state of science, the molecular constitution of bodies and the mode of arrangement of their elements, are problems yet unsolved, even with respect to the most simple organic substances; and *à fortiori*, unsolvable with regard to those which are complex. (*Traité de Chimie*, 1861, ii. p. 463.)

The non-oxygenated oils of the vegetable kingdom, present a remarkable isomeric series. In their ultimate constitution they consist of hydrogen and carbon, forming the series of hydrocarbons. Thus oil of turpentine, one of the series, has the formula $C_{20}H_{16}$. The oils of lemons, oranges, bergamot, camomile, cloves, and thyme are represented by the same formula ($C_{20}H_{16}$); and the differences existing among these oils can only be referred to a different molecular arrangement of the carbon and hydrogen.

This complex atomic constitution leads to results which may be regarded as peculiar to organic chemistry—namely, the variety of artificial products which may be obtained from them by different methods of treatment. Thus, in reference to the effects of *heat*, some are volatilized without decomposition (benzoic acid); others are entirely decomposed, as gum, starch, and sugar, yielding compounds which vary in their nature, according to the temperature applied; while a third class, at a heat below redness, are converted into new and stable compounds, simply by the loss of the elements either of water or of carbonic acid. When gallic acid is converted into pyrogallic acid by heating it to about 410°, carbonic acid is evolved, and the new acid is sublimed in crystals:—

$$\underbrace{C_{14}H_6O_{10}}_{\text{Gallic acid.}} = \underbrace{C_{12}H_6O_6}_{\text{Pyrogallic acid.}} + \underbrace{2CO_2.}_{\text{Carbonic acid.}}$$

Again, when pyrogallic acid itself is heated to a still higher temperature (482°), it is resolved into water, and a black amorphous insoluble compound, which is called metagallic or gallulmic acid:—

$$\underbrace{C_{12}H_6O_6}_{\text{Pyrogallic acid.}} = 2HO + \underbrace{C_{12}H_4O_4}_{\text{Metagallic acid.}}$$

So, when malic acid is converted by heat into maleic acid, water is evolved. Thus—

$$\underbrace{C_8H_6O_{10}}_{\text{Malic acid.}} = \underbrace{C_8H_4O_8}_{\text{Maleic acid.}} + 2HO$$

The organic acid is thus entirely transformed, partly into a new pyrogenous acid, and partly into water or carbonic acid, without leaving, in a carefully conducted experiment, any trace of carbon in the retort. (PELOUZE.) The influence of heat in causing the re-arrangement of the elements of hydrated cyanate of ammonia, and its conversion into a neutral organic base, urea, has been already pointed out (p. 18). The conversion of starch and gum into sugar, and the transformation of cane-sugar into grape-sugar, when these substances are heated, or merely agitated with diluted acids, furnish other illustrations of the facility with which a new arrangement of atoms is produced, and tend to confirm the corectness of chemical views regarding the isomeric constitution of these bodies. The production of oxalic acid by treating sugar with nitric acid, or by acting on sawdust (woody-fibre) with potassa at a low temperature, proves not only the facility of change, but the very different chemical methods by which this change may be brought about. It would be easy to multipy instances of this kind, by referring to the action of some of the metalloids, as well as of their compounds, on organic substances. The range of organic chemistry has been of late years almost infinitely extended to the application of this simple method of research.

EDUCTS AND PRODUCTS.—The *products*, or those substances which result from artificial processes, are far more numerous than the *educts*, or proximate principles of which organic compounds are considered to be formed. These educts, which, as their name implies, may be extracted in an unaltered state, are the immediate or *proximate* principles of the vegetable or animal structure; and the means of separating them, or determining their proportion, constitutes an important branch of chemical research, known as *proximate analysis*. The elementary analysis of wood would merely indicate the presence of carbon, hydrogen, and oxygen (C,H,O): but its principal proximate constituents, or the *educts*, which may be extracted from it without change of properties, are gum, resin, and woody fibre, each of which would yield the same elements as the original wood, but in proportions varying slightly with each substance. If we compare Boussingault's analysis of the grain of wheat and of wheat-straw, we shall find but little difference in the proportion of the elements, although the former contains nutritious principles in the form of starch, gluten, dextrine, and sugar; while the latter consists chiefly of woody fibre, and contains but little nutrient matter.

	Grain of wheat.	Wheat-straw.
Carbon	46·10	48·40
Hydrogen	5·80	5·30
Oxygen	43·40	38·95
Nitrogen	2·30	0·35
Ash	2·40	7·00
	100·00	100·00

Educts, when separated, are possessed of peculiar physical and chemical properties by which they may be identified, and it is to the accurate study of these, as well as a knowledge of their elementary composition, that we owe the numerous additions which have been made to this branch of science. To take a simple illustration, *gum* is an educt: its constitution is similar to that of cane-sugar ($C_{12}H_{11}O_{11}$). When 1 part of gum is boiled with 4 parts of nitric acid (sp. gr. 1·38) and 1 part of water, it loses 3 atoms of hydrogen, acquires 3 atoms of oxygen, and is transformed into a white uncrystalline and comparatively insoluble substance—mucic acid ($C_{12}H_8O_{14}$,2HO). This compound, when moderately heated, is converted, like gallic acid, into a volatile pyrogenous acid, while carbonic acid and water escape.

$$\underbrace{C_{12}H_8O_{14}2HO}_{\text{Mucic acid.}} = \underbrace{C_{10}H_3O_5,HO}_{\text{Pyromucic acid.}} + \underbrace{2CO_2}_{\text{Carbonic acid.}} + \underbrace{6HO}_{\text{Water.}}$$

When the isomeric compound, cane-sugar ($C_{12}H_{11}O_{11}$), is similarly treated—*i. e.*, when 1 part of sugar is boiled in 8¼ parts of nitric acid (sp. gr. 1·38), and the liquid is concentrated—an acid of a totally different nature is obtained, namely, the oxalic (C_2O_3). Both gum and cane-sugar are convertible into grape-sugar, $C_{12}H_{14}O_{14}$, or $C_{12}H_{12}O_{12}2HO$, by the same process, *i. e.*, by heating them in diluted sulphuric acid. In this conversion, three atoms of water are fixed. From gum, therefore, as an educt, we may obtain mucic acid, pyromucic acid, and grape-sugar, as products; and from cane-sugar, oxalic acid, and grape-sugar. By slightly varying the methods of treatment, other products may be obtained. Thus woody fibre, or cellulose ($C_{12}H_{10}O_{10}$), when heated with potassa, is converted into oxalic acid; but when treated with cold sulphuric acid it is transformed into grape-sugar. Under the action of nitric acid, water is produced at the expense of a part of the hydrogen; and for each atom of hydrogen lost, one atom of nitrous acid (NO_4) enters into combination. Gun-cotton is the result of this chemical substitution of nitrous acid for hydrogen.

Some bodies which exist naturally in the vegetable structure, and are regarded as educts, may be artificially produced by a reaction of mineral on organic substances. In all cases, however, either an organic substance, or a body derived from the organic kingdom, is indispensable to this conversion. Hydrocyanic acid may be regarded as an organic product. The materials for its production, on contact with water, exist in the bitter almond, the kernels of the peach, the seeds of the apple, and other fruits of a similar kind, as well as in the root of the plant from which tapioca is obtained (*Jatropha manihot*), and in the shoots and leaves of the laurel and bay-trees. The principal sources of hydrocyanic acid are, however, certain metallic cyanides (page 265). But these compounds have an organic origin: they are the products of a reaction of organic upon inorganic substances; hence the production of hydrocyanic acid by their decomposition furnishes no exception to the remark above made. Under this point of view, the production of artificial urea from hydrated cyanate of ammonia is simply a conversion of cyanic acid (a derivative of an organic substance) into another organic compound. By no processes yet known, can gum, starch, or sugar, be produced from their elementary constituents (CHO); and, by the production of alcohol from a mixture of sulphuric acid, olefiant gas, and water, Berthelot has merely proved that a hydrocarbon of organic origin, or one derived from organic matter, is capable of being converted into another organic product. Olefiant gas is obtained by a reaction of sulphuric acid on alcohol (page 258), and Berthelot's ingenious experiment proves that when olefient gas is dissolved in sulphuric acid, and this is mixed with water and distilled, alcohol is reproduced. This is a simple case of synthesis. Another source of olefiant gas is coal; but of the organic origin of this substance no doubt can be entertained.

There appears to be scarcely a limit to this power of transforming one organic substance into another, and thus producing compounds analogous to educts, or those which are formed by nature. Oxalic acid is a natural constituent of the leaves of sorrel and of the rhubarb plant (*Rheum rhaponticum*); but, as above stated, it is an artificial product of the reaction of potassa on woody fibre, and of nitric acid on sugar. The formic acid, which exists naturally in the body of the red ant, and as there is reason to believe in the poison of the wasp and bee, is readily procured by the action of sulphuric acid and peroxide of manganese on gum, starch, sugar, or tartaric acid. It may also be procured by a reaction of peroxide of lead on tartaric acid. Glucose, or grape-sugar, which exists in the grape and other fruits, is produced in large quantity by the reaction of diluted sulphuric acid on starch. By other processes, succinic acid, which is naturally contained in amber, is produced by the action of nitric acid on certain fatty substances: butyric acid is a product of the fermentation of grape-sugar; and lactic acid is produced by the fermentation of grape-sugar and sugar of milk.

The instability which characterizes organic products seems in a great measure to arise out of the peculiarities of their atomic constitution; and accordingly we find that, under circumstances in which inorganic compounds remain unchanged, organic substances are subject to a variety of changes, the tendency of these being generally such as to terminate in the production of binary compounds. The complicated phenomena of fermentation, putrefaction, and decay (page 89) will illustrate these tendencies; and the very existence of organization is intimately dependent upon them. In these cases several intermediate stages are often passed through, but the principal ultimate results are the production of *carbonic acid*, *water*, and *ammonia*. These form the chief food of vegetables; and when absorbed either from the atmosphere or from the soil, they furnish carbon, hydrogen, oxygen, and nitrogen, again to be elaborated into "proximate organic principles" by the vital powers of the plant. It is only under such conditions, that vegetables can assimilate the materials of which their fabrics are built up; and, in fact, so combine them as to form the proximate components of the animal frame; while, on the other hand, the animal functions work in an opposite direction, and produce the above-mentioned binary compounds. Thus are the tendencies of the animal and vegetable kingdoms found to work in diametrically opposite directions: the former decomposing and destructive, the latter composing and regenerative. Strictly speaking, the two kingdoms may be regarded as supplementary to each other; that which the vegetable ejects, is necessary to animal existence; and that which the animal eliminates, is necessary to the vegetable. No plant could grow and thrive without carbonic acid and water, and no animal could live without oxygen. The vegetable, therefore, lives by a process of deoxidation, and the animal by a process of oxidation. The vegetable may be regarded as the living chemical laboratory which prepares the food for the animal. Water and chloride of sodium appear to be the only mineral substances which are employed as food by animals. Other substances used as food, are derived either from plants or animals.

SPONTANEOUS CHANGES.—Probably there is no greater difference between organic and inorganic substances than that spontaneous tendency to change which is manifested by the former, and to which the term *fermentation* is somewhat loosely applied. By exposure to air, and at a moderate temperature, in the presence of a body which is called a *ferment*, sugar is spontaneously converted into alcohol and carbonic acid; and alcohol into acetic acid and water. There are other remarkable conversions of an analogous kind, by which gallic, lactic, butyric, and hydrocyanic acids, are produced from substances which either do not originally contain them, or contained them only in small quantity. These changes frequently consist in the simple absorption or fixation of oxygen. Thus the essential oil of bitter almonds is converted, by exposure to air, into benzoic acid (page 86); ether, from being neutral, is partially changed into acetic acid, and acquires an acid reaction. The gallic and pyrogallic acids when dissolved in water and exposed to air, rapidly absorb oxygen, and are converted into dark-brown oxidized compounds. This change takes place with great rapidity when the acids are mixed with an excess of any alkaline base. Chemists employ a solution of this kind as a ready method for absorbing oxygen (page 91). When pyrogallic acid is dissolved in neutral ether, it has no acid reaction if kept from air; but when oxygen has free access to it, litmus-paper moistened with the liquid, becomes reddened by the absorption of this element, showing that an acid is produced, although in the absence of pyrogallic acid, the liquid simply evaporates without reddening the paper. Woody fibre is transformed by oxidation into a brown insoluble compound called humus, and carbonic acid is evolved, constituting that condition which has been described as *eremacausis* (page 89). In place of the oxygen entering into combination with the new compound, or being evolved as carbonic acid, it may operate by removing part of the hydrogen and producing water. The transformation of white to blue indigo by exposure to air, is considered to be dependent on a change of this kind:—

$$\underbrace{C_{16}H_6O_2N}_{\text{White indigo.}} + O = HO + \underbrace{C_{16}H_5O_2N}_{\text{Blue indigo.}}$$

The operation of the *ferment* in some of these metamorphoses, appears to be of a catalytic kind (page 54). It takes no absolute share in the changes, but it induces an altered molecular arrangement in other bodies. In reference to the oxidation of bodies, the ferment may even be replaced by a mineral substance—platinum-black—which has the power, under a moderate access of air, of rapidly transforming alcohol into water and acetic acid ($C_4H_6O_2+O_4=3HO+C_4H_3O_3$); and of converting wood-spirit into water and formic acid; ($C_2H_4O_2+O_4=3HO+C_2HO_3$). These facts show that a ferment, in certain cases, operates, like platinum-black, merely as a medium for transferring oxygen.

The living animal body furnishes numerous illustrations of the facility with which certain organic substances pass and repass into each other. Among these, there is probably none more striking than the conversion of benzoic acid ($C_{14}H_5O_3$) into hippuric acid ($C_{18}H_8O_5N,HO$). A small quantity of benzoic acid, when taken into the system, is eliminated in the urine as hippuric acid. The hippuric acid naturally contained in the urine of the horse, slowly disappears, and is spontaneously changed, by a species of fermentation, into the benzoic. The condition of the animal appears to favor the production of one or the other acid, according to circumstances. Thus when the animal is kept at rest, hippuric acid is abundant: but when violently exercised, this is replaced by the benzoic. This transformation, whether viewed as the result of changes in the living animal, or of fermentation out of the body, is the more remarkable, inasmuch as the two acids have no isomeric relations, and appear to have no analogous composition. In some instances we obtain a key to this conversion, and can imitate the process. When a mixture of gelatinous starch is heated for a few minutes to a temperature of about 90°, with a small quantity of saliva, or of the vegetable principle *diastase*, it will be found that the starch has become partially converted into grape-sugar by a fixation of the elements of water.

It is worthy of remark that sulphurous acid and sulphites have a tendency to prevent these changes, probably by absorbing and removing oxygen. It has been long known that sulphurous acid had the power of arresting the conversion of sugar into alcohol, and of alcohol into acetic acid; but it operates with equal effect in preventing the conversion of starch into sugar by saliva and diastase. Some of these spontaneous changes are of a complex character, and take place in close vessels irrespective of the absorption of oxygen. Thus pyroxyline (gun-cotton or paper) is sometimes resolved, without any apparent cause, into nitrous and hydrocyanic acids.

PROXIMATE ANALYSIS.—An organic substance frequently contains a certain proportion of *water* as well as of *mineral matters*. The leaves of plants contain from 80 to 85 per cent. of water, and the soft animal tissues contain a very large quantity (p. 130): to the presence of this water their physical properties are mainly due. The driest vegetable powders contain a certain percentage of it, which must be removed before a correct analysis can be made. The methods of removing water, and determining the quantity present, have been elsewhere described (p. 134).

The *mineral* substances are sometimes in large proportion in the vegetable and animal structure. Bone contains about 67, and the teeth 70 per cent. of mineral matter, in the form of phosphate and carbonate of lime. Shells, and other solid structures of the like nature, are chiefly constituted of carbonate of lime, cemented by animal matter. In certain infusoria, *silica* is very abundant: this substance is also an important constituent of the epidermis of the reeds and grasses. It forms from 13 to 50 per cent. of the ashes of some species of plants (p. 281). It is associated with oxide of iron, and sometimes with traces of manganese. Certain salts of lime, potassa, soda, and magnesia, are the principal mineral constituents of organic substances. The alkalies are generally found in the ash, combined with carbonic acid (a product of the combustion of organic acids) and with sulphuric acid; or in the state of chlorides, iodides, and bromides of the respective metals. The alkaline earths are also found as carbonates, but frequently associated with the phosphoric, sulphuric, and silicic acids. Lime and oxide of iron exist more or less in the ashes of all organic substances; and the metals iron and manganese (the latter rarely) are found in the residue of combustion, as oxides. These mineral ingredients, although generally small when compared with the weight of the organic constituents, appear to be of essential importance to the life of plants, and to the structure of the skeleton in animals. They serve, in the vegetable kingdom, to build up the cell-walls for the reception of the organic principles, and they give firmness and strength to the vegetable structure. Potassa and soda are found abundantly in succulent plants. These alkalies exist more or less in combination with vegetable acids in all plants; and it is to the presence of their carbonates that the alkaline reaction of the ashes of vegetables is due. Potassa is more abundant in inland, and soda in marine plants; certain vegetables, such as the *Armeria maritima*, *Cochlearia officinalis*, and *Plantago maritima*, produce chiefly potassa when they grow in inland districts, and soda when near the sea-coast. It is probable that soda is never entirely absent from the ashes of vegetables. Although it cannot be detected by ordinary processes of analysis in the ashes of many inland vegetables, including the foliage of trees, its presence has been revealed in every instance by the photo-chemical process of Bunsen and Kirchoff. A quantity of sodium, amounting to less than the 20,000th part of the weight of the ash, readily admits of detection by spectral analysis. Soda is the principal alkali of animal compounds: as chloride of sodium, it is found in the ashes of most animal solids and liquids. Lime in combination with phosphoric acid is found in all the cereal grains, as well as in potatoes, turnips, chiccory, and other roots. The oxalate and carbonate of lime, in a crystalline state, are found sometimes in the cells of plants, constituting *raphides.* Crystals of oxalate of lime are found abundantly in the root of rhubarb, and in certain cactuses. Iodine and bromine exist as iodides and bromides, not only in marine, but in many land plants; and fluorine has been detected as a constituent of scurvy-grass (*Cochlearia officinalis*), and in other plants growing near the sea. The only vegetables which, according to Mulder, yield no mineral ash or residue, are the mould-plants, formed in saccharine and acid liquids. They consist of cellulose with nitrogenous substances. Like the *acalephæ*, or jelly-fish, of the animal kingdom, they are chiefly constituted of water, and yield, on drying, merely a trace of solid matter. The proportion of mineral matter contained in an organic substance varies with its nature. We have elsewhere given the proportions of ashes yielded by different kinds of wood (p. 239). By reference to the analysis of wheat and straw (p. 498), it will be seen that the proportion in the straw is threefold that of the grain. Certain educts, when separated from the vegetable by artificial processes, may be obtained so pure that, on incineration, they leave no mineral matter—*e. g.*, starch and sugar; others, such as gum, are always associated with a large quantity of lime, as well as oxide of iron. The mineral matters found in vegetables, are considered to have a telluric origin; *i. e.*, they are supposed to be derived from the soil. Sulphur and phosphorus, in combination with oxygen, united to bases, as sulphates and phosphates, are found in the earth; and chlorine, combined with sodium, is present in all soils and in all waters. It is probable that plants growing near the sea-side derive a large portion of the soda which they contain from the diffusion of the chloride in watery vapor in the atmosphere. Marine plants and animals derive this salt, chloride of sodium, carbonate of lime (as coral or shell), as well as the iodides and bromides of the alkaline metals, directly from sea-water. The following list comprises the principal inorganic constituents of vegetable and animal substances: $S(SO_3)$. $P(PO_5)$. $Si(SiO_3)$. $Ca(CaO)$. $Mg(MgO)$. $K(KO)$. $Na(NaO)$. Cl. I. Br. F. $Fe(Fe_2O_3)$. and $Mn(MnO)$.

The chloride of *rubidium* has been detected by M. Grandeau in the saline waters derived from beet-root, associated in minute quantity with chloride of potassium. It has also been found in the ashes of tobacco, tea, coffee, and in the crude tartar derived from the grape. The colza, cacao, and sugar-cane, contained none, although some of the ashes were rich in potassium. By spectral analysis, *lithium* has been detected in the ashes of seaweed, of the vine, tobacco, and of numerous other plants growing on the granitic soil of Germany. It is stated that it has also been found in the ashes of milk, blood, and muscular tissue. Dr. Cameron did not detect it in cereal plants, and in some fuci which he examined; but he found that when lithia was added to the soil, the ashes of barley contained this alkali, which had been apparently substituted for soda in the plant (*Chemical News*, May 31, 1862). It is remarkable that alumina (Al_2O_3) which is a large constituent of every soil, is rarely found in the ashes of vegetables, except as an accidental ingredient. The analyses hitherto made show that alumina is not an essential constituent of plants, and that it is very rarely present.

Although plants appear to have generally a power of rejecting noxious ingredients, yet in certain cases, substances of a poisonous nature are taken from the soil by the roots, and are distributed through their tissues. The metals thus absorbed, appear to be deposited there, without injuring the growth or vitality of the plant. We have found by direct experiment that the seeds of mustard and cress, grown on a soil containing the disintegrated slag of old lead-works, took up a sufficient quantity of lead to allow its presence to be readily determined in the grown plants. We also found lead in the ashes of many plants and shrubs, and of the grass growing on lead-slag, in the valleys of the Mendip hills. Care was taken to remove any particles of the soil adhering to the plants. Dr. Cameron states that he invariably found lead in the plants grown near lead-smelting works at Ballycorus, county of Dublin (*Chemical News*, June, 1862, p. 315). Dr. Wilson has made a similar observation; and further, that herbage thus impregnated with lead, may be a cause of lead-poisoning in cattle (*Edinburgh Monthly Medical Journal*, 1852, vol. xiv. p. 386). The question has been raised whether plants can thus imbibe arsenic from the soil; and this is of some importance, inasmuch as arsenical sulphuric acid is largely employed in the manufacture of certain manures. The only recorded instances of the absorption of this mineral, are in some observations made by Dr. Davy and Mr. Horsley. They found that turnips and other vegetables grown on soils on which arsenicated manures had been placed, acquired an impregnation of arsenic (*Philosophical Magazine*, August, 1859, p. 108). Some of the lower kinds of plants (confervæ) readily grow in certain metallic solutions, which are poisonous to animals. A solution of tartar emetic exposed to air becomes speedily covered with confervoid growths of a peculiar kind. Mould-plants are observed to flourish in solutions of tartaric, citric, gallic, and tannic acids, and their compounds, but not in a solution of oxalic acid.

With respect to the inorganic elements found in the animal kingdom, if we except the zoophytes and marine mollusca, these elements may be traced to the food of the animal, and not to the medium in which they live. Thus all terrestrial animals derive their support either from other animals or from vegetables; hence, except from accidental circumstances, the inorganic compounds found in animals are the same as those which exist in vegetables.

The separation of *mineral* matters from an organic substance may be effected by burning a known weight in a platinum crucible. The carbon, oxygen, and hydrogen, are thus removed, and the residue, which is a light, porous, white, or (if iron is present) réddish-colored ash, can be readily weighed. It will probably be found to contain salts, some of which are soluble in water, and others only dissolved by acids. The larger proportion of the ash is generally insoluble in water. Thus of 100 parts of the ashes of the oak, only 15 parts are dissolved by water; of the ashes of the box, 24 parts; and of the ashes of the fir, 17 parts. The acids and bases may be sought for by the rules laid down at pp. 349 and 492. It has been suggested that nitric acid should at once be employed for the removal of these mineral substances from the vegetable. In a few cases this may be resorted to; but the most certain method of separation is that of incineration. The presence of mineral matter in any organic substance may be readily detected by heating a portion of it on thin platinum foil, or in a platinum capsule. If there is any difficulty in consuming the carbon, it may be finely powdered, mixed with its weight of red oxide of mercury, and heated either in a glass tube or porcelain capsule. The proportions of water, mineral, and organic matter, in 100 parts of the fresh leaves of the lettuce and nettle, and of the lime, ash, and elm-trees, are derived from recent experiments:—

	Lettuce.	Nettle.	Lime.	Ash.	Elm.
Water	96·6	79·60	80.	75·83	70·
Mineral matter	0·6	2·96	2·	1·66	2·
Organic matter	2·8	17·44	18·	22·51	28·
	100·0	100·00	100·	100·00	100·

The water was determined by spontaneous desiccation and subsequent drying at 212° ; and the ash by careful incineration in platinum : the ash in each case was nearly white. It was more or less alkaline, and was found to contain carbonic, sulphuric, and traces of phosphoric acid, chlorine, potassa, lime, magnesia, and oxide of iron. The elm and nettle-leaves contained the largest, and the lime and ash-leaves the smallest proportion of lime and oxide of iron. The greatest amount of phosphoric acid was found in the nettle, associated with lime. The color-test to flame gave not the slightest indication of the presence of soda in any of the leaves. Probably by spectral analysis both sodium and rubidium might have been found.

The *proximate analysis* of an organic substance may be generally effected by various solvents, such as ether, alcohol, or water, successively applied ; and occasionally sulphide of carbon, benzole, oil of turpentine, or chloroform, may be employed as substitutes for ether. Ether, which should be used first, is a solvent of fatty and waxy substances, as well as of resins, camphor, and some essential oils. Alcohol is a solvent of resins, and of a variety of bodies, upon which ether has but little action ; while water, either cold or hot, is an important solvent of many neutral vegetable principles, such as gum, sugar, or starch. Vegetable alkalies may be dissolved by diluted acetic, hydrochloric, or sulphuric acid ; and are thus obtained in a state for further separation by potassa, ammonia, or lime. Vegetable acids admit of separation by potassa, lime, oxide of silver, or lead ; and from the compounds thus produced, the acid may be procured by a diluted mineral acid, or by the decomposition of a vegetable salt of lead by sulphuretted hydrogen. The solvents above mentioned, often remove several substances at one time. Those which are of a crystalline nature may be separated either by cooling or concentrating the solution to different degrees, or by varying the solvent. The new process of *dialysis* may be also employed for the separation of salts from organic matter diffused in water (pp. 46, 134).

Fractional distillation, as applied to volatile liquids, admits of a more or less perfect separation of these liquids, by collecting the products which are condensed at a fixed temperature, or within a range of a few degrees. Thus, rectified coal-naphtha consists of a series of volatile oils which boil at temperatures varying from 140° to 342°. By condensing the vapors evolved at different temperatures, at which the thermometer remained fixed, Mansfield found that this liquid might be resolved into five oils, having different boiling-points, and possessed of different properties. The oil which boils at 176°, and is condensed below that temperature, is well known as an important product, under the name of benzole ($C_{12}H_6$). To this method of separation we owe the production of paraffine from the tarry oils obtained by the distillation of coal or bituminous schist at a low temperature. These remarks apply to the preliminary separation of substances for a further analytical investigation. It would be impossible to lay down any general rules for the qualitative and quantitative examination of the bodies thus obtained in solution, or as a result of distillation. The properties of each organic compound must be separately studied, and the tests for its detection, and the processes required for its separation, must be well understood, before a successful proximate analysis can be made. The difficulties with which a chemist has to contend are, that organic substances are liable to undergo changes by mere contact with simple chemical reagents, and that the means of perfect separation by precipitants are much more limited than in mineral chemistry.

CHAPTER XLIV.

ULTIMATE OR ELEMENTARY ANALYSIS.

ORGANIC CONSTITUENTS.—Assuming that the hygrometric water has been removed from an organic substance, and that the proportion of mineral matter, if present, has been determined, the next stage is to ascertain the nature and proportion of the organic constituents. These are, in the vegetable, chiefly three, represented by carbon, hydrogen, and oxygen, occasionally associated with nitrogen, sulphur, and phosphorus. In the animal, they are commonly four—carbon, nitrogen, hydrogen, and oxygen; and more frequently than in the vegetable, associated with sulphur and phosphorus. *Carbon* is the only element which appears to be essential to an organic compound. Gmelin has justly observed that each of the other elements may be absent from particular compounds; but no compound, which, in all its relations, deserves the name of organic, is destitute of carbon. Further, organic compounds are distinguished from the carbon compounds of the inorganic kingdom, by containing more than one atom of this element. The atoms of carbon in organic formulæ are in pairs, or in even numbers. The carbon is frequently in such proportion as to be equal to the combined weights of oxygen and hydrogen: it is generally in large excess, and is estimated to form from one-half to two-thirds of the weight of dried organic matter. It constitutes 42 per cent. of sugar, 52 per cent. of the weight of alcohol, and 87 per cent. of the weight of oil of turpentine. The great source of carbon to the vegetable, is the carbonic acid diffused through the atmosphere (p. 149.) Although the proportion present in air, is relatively small, it is very great when the bulk of the atmosphere is regarded. This gas is absorbed by the leaves of plants, and while carbon is partly retained, oxygen, carbonic oxide, and carburetted hydrogen (in the proportion of 1·11 c.i. to 100 of oxygen) are eliminated (p. 245). Boussingalt found that when air was passed over the fresh leaves of the vine, the carbonic acid was absorbed. The influence of light appears to be necessary for the elimination of these gases. The roots of plants also take up a portion of carbonic acid in a state of solution in water.

Test for an Organic Compound.—In determining the question whether a substance is of an organic or inorganic nature, a chemist seeks for the presence of carbon. No organic substance contains a sufficient quantity of oxygen to consume the whole of its carbon and hydrogen; hence if the suspected solid is heated in a close vessel, so that air can have no access, a black or carbonized residue will remain. The experiment may be readily performed by heating the substance in a small glass tube. If organic—*e.g.*, starch—it will be carbonized: if inorganic—*e.g.*, sulphate of lime—it will remain unchanged. Volatile bodies—such as the oxalic and benzoic acids, alcohol, ether, and acetic acid—require a different method of treatment. Some are entirely, and others are only partly, volatile. Anhydrous oxalic acid, too, presents this peculiarity: the oxygen is in sufficient quantity to transform the carbon into carbonic acid and carbonic oxide, but as an independent acid it always contains an atom of water. No inorganic compound leaves a residue of carbon when heated under similar circumstances.

Sulphuric acid is sometimes employed as a medium for testing the organic nature of an unknown solid. When the substance is heated with an excess of the acid, the mixture is blackened by the liberation of the carbon, and sulphurous acid is evolved as a result of the decomposition of a part of the acid employed. Sulphuric acid, however, produces peculiar effects with many organic products: it dissolves indigo, forming a blue solution; and gallic acid, forming a rich crimson-colored liquid; it produces red-colored compounds with veratria, certain resins, and oil of bitter almonds; and while it carbonizes many bodies, it dissolves others, such as citric acid, with scarcely any change of color. On the whole, the effect of heating the compound in a close vessel furnishes the most reliable evidence of its organic nature.

Carbon.—If we have satisfied ourselves, by the production of a carbonaceous residue, that the substance is organic, we may next proceed to determine, by an accurate chemical method, not only the presence, but the proportion of carbon present. The substance, well dried and finely powdered, is mixed with dried chromate of lead, or black oxide of copper, and introduced into a tube which is connected with two balanced tubes, the first containing broken chloride of calcium for drying the gaseous products, and the second a strong solution of potassa, either by itself, or diffused through dry pumice (p. 149). When the mixture is strongly ignited, the carbon of the organic substance is entirely converted into carbonic acid: this is dried by the chloride of calcium, and the gas itself is absorbed by the potassa. The increase of weight in the potassa indicates the amount of carbonic acid present. 100 parts of carbonic acid represent 27·2 parts by weight of *carbon* (C). The chromate of lead is preferable to the oxide of copper, as at a high temperature it fuses and incloses the organic matter, thus insuring the complete oxidation of the carbon present. The changes which take place will be readily understood. The oxide of copper is simply deoxidized, $2CuO + C = CO_2 + 2Cu$; but the chromate of lead is reduced to subchromate and sesquioxide of chromium, $4(PbO,CrO_3) = 4PbO,2CrO_3 + Cr_2O_3 + O_3$. The oxygen liberated is taken by the carbon. Unlike the black oxide of copper, this compound evolves oxygen by the mere effect of heat.

The oxide of copper or chromate of lead is deoxidized, not only by the carbon, but by the hydrogen of the organic matter: and carbonic acid and water are produced. The water is absorbed by the chloride of calcium. The production of carbonic acid under these circumstances, furnishes of itself a good test of the presence of organic matter. Thus, in place of heating the organic compound in a close vessel, it may be mixed with oxide of copper and heated at once in a small tube bent at an angle and drawn out in a capillary form at the open end. This may be broken off and dipped into a small quantity of lime-water contained in a tube or watch-glass. If carbon is present, carbonic acid is produced, a fact indicated by a milky precipitate in the lime-water. A mere trace of carbon in a substance thus easily admits of detection.

Hydrogen.—This element is commonly in small proportion by weight; but there is a large class of organic compounds which are formed entirely of hydrogen and carbon, the carbon always preponderating. Hydrogen forms about 6 per cent. of sugar, and 13 per cent. of alcohol and oil of turpentine, the latter being of pure hydrocarbon. There is no direct test for the presence of this element in organic matter. The proof of its presence in a dried organic substance is derived from the production of water, either by simply heating the solid to a certain temperature, or by igniting it in a tube with black oxide of copper or chromate of lead. In this case the deoxidation is effected by hydrogen as well as by carbon, and if the substance has been properly dried at 212°, and the oxide of copper or chromate of lead has been well dried, all the water carried over and condensed in the chloride of calcium tube will represent the amount of hydrogen in the organic substance. The chromate of lead, when it has been fused and powdered, is much less absorbent of water than the oxide of copper; hence it gives more correct results for hydrogen.

Inflammable liquids containing hydrogen, such as alcohol and ether, produce a large quantity of water by combustion in air. The method of determining the presence and amount of hydrogen has been described above under *Carbon*, and additional details will be found at pp. 114 and 134. The increase of weight in the chloride of calcium tube, which arrests the water, divided by 9, indicates the amount of hydrogen present. Thus, 100 parts of water are equivalent to 11·1 H.

The hydrogen existing in vegetable substances is, no doubt, chiefly derived from the deoxidation of water, either as it is diffused in vapor through the atmosphere, or taken up from the soil. This element is never found in the atmosphere in a free state, but some of its compounds—namely, ammonia and light carburetted hydrogen—have been detected in air in small quantities; and some portion of the hydrogen of the vegetable structure may be derived from these sources, the nitrogen and carbon being at the same time appropriated. The vital power which can separate hydrogen from oxygen can also separate this element from nitrogen and carbon: the oxygen eliminated from the decomposed water is supposed to be ozonized, like that which is set free by the electrolysis of water (p. 101).

Oxygen.—This element, next to carbon, is the principal constituent by weight of organic matter. In some compounds, as in vegetable acids, it is in greater proportion than carbon. It constitutes 66 per cent. of anhydrous oxalic acid, 52 per cent. of sugar, and 34 per cent. of alcohol. In the case or oxalic acid, it is associated with carbon only; but in sugar, alcohol, and the greater number of vegetable principles, it is combined with hydrogen, and sometimes with nitrogen and sulphur. Some of the alkaloids, acids, and neutral compounds contain none—*e. g.*, nicotina, aniline, hydrocyanic acid, and oil of turpentine. There is no direct test for the presence of oxygen in organic substances, if we except the production of carbonic acid and water by heating them out of contact of air. The oxygen is then consumed by the hydrogen of the substance, and water is produced as well as carbonic acid. The general principle on which the determination of the presence and amount of oxygen is based consists in the separation and quantitative estimation of the other constituents, and in the deduction of the sum of these from the amount of dry organic matter employed in the experiment. If the substance examined was perfectly dry and pure, and the other elements have been accurately weighed, this method will give a sufficiently correct result; but any errors on these points will add to or diminish the amount of oxygen. When the substance consists of carbon, hydrogen, and oxygen only, the results are generally satisfactory; but when nitrogen, sulphur, and phosphates are present, there is greater difficulty attending the correct estimation of the oxygen. The oxygen found in organic substances is probably derived, not only directly from the atmosphere, but indirectly from the oxidized products —carbonic acid and water—which are diffused through it.

Nitrogen.—This element, although most abundantly found in animal substances, is an important constituent of many vegetable compounds. Albumen, fibrin, and casein of both kingdoms contain it in a large proportion.

It exists in the sap and juices of vegetables: it is present in many alkaloids, in indigo, in bases such as aniline and nicotine; also in amygdaline, in hydrocyanic and carbazotic acids, and in a great variety of artificial products. Compounds of nitrogen and hydrogen, or of nitrogen and oxygen, are not met with among organic substances. Ammonia, which is constituted of nitrogen and hydrogen, is not an organic substance, but the product of the decomposition of organic matter. Nitrogen is associated with carbon in cyanogen and its compounds, with sulphur in oil of mustard, and with sulphur and phosphorus in albumen, fibrin, and other organic principles.

Organic substances which contain this element and a sufficient quantity of moisture, undergo changes to which the term *putrefaction* is applied. One of the most abundant products is ammonia, which is derived from the nitrogen uniting with hydrogen in the nascent state.

The presence of nitrogen may in general be determined by heating the dried substance in a close tube: ammonia, in combination with carbonic or hydrosulphuric acid, is distilled over with water among the first products. The alkaline gas may be identified by its pungent odor, and by its reaction on test-paper placed in the mouth of the tube, or by any of the usual tests. The substance may be heated in a tube, with hydrate of potassa or calcined soda-lime, finely powdered: in either case the nitrogen present is entirely set free as ammonia. The alkaline bases operate by fixing any acid that may be produced. For another method of detecting this element, *see* pp. 142, 143. Even a diluted solution of potassa, at a moderate heat, will in some cases destroy the substance and produce ammonia. Among alkaloids, strychnia and morphia resist the action of a solution of potassa which is sufficient to decompose atropia, aconitina, and hyoscyamia. Morphia, or strychnia, when heated alone, evolves ammonia, showing that nitrogen is a constituent of these alkaloids; but their salts give off no ammonia when heated, unless they are mixed with 4 or 5 parts of hydrate of potassa or dry soda-lime. Caoutchouc, when heated in a reduction-tube, evolves ammonia; gutta-percha does not. When nitrogen is absent, the organic solid commonly evolves an acid (acetic), the vapor of which reddens litmus-paper. Thus dextrine, gum, or woody fibre, when heated strongly in close vessels, evolves acetic acid. Non-nitrogenous are thus distinguished from nitrogenous substances: If we heat in a tube a small quantity of Russian isinglass, ammonia is copiously evolved; but if we substitute for this the substance called Japanese isinglass (*Gelidium corneum*) an acid vapor escapes. This substance contains no nitrogen, while the Russian isinglass contains it in large proportion.

The vegetable is supposed to derive its nitrogen chiefly from ammonia diffused through the atmosphere, or carried by rain into the soil. The very small proportion of ammonia found in air (p. 150) may appear to be insufficient as a source of nitrogen for plants; but vegetables have the power of extracting and appropriating their elements, even when diffused in such minute traces as not to be revealed by ordinary reagents. Rubidium has been detected in the salts obtained from beet-root, but none has hitherto been found in the soil. A similar fact has been noticed with regard to marine plants; they have a power of accumulating and fixing iodine in their tissues; but in the sea-water in which they flourish, it is difficult to detect, by chemical tests, any traces of iodine, even when a large quantity is made the subject of experiment. Although nitrogen is an abundant constituent of the atmosphere, there is no evidence that vegetables procure it directly from this source. As hyponitrite or nitrate of ammonia (the result of the oxidation of the elements of air and aqueous vapor by ozone or electricity), nitrogen in a combined state is not only diffused in the atmosphere, but carried by rain into the soil. According to the recent views of Schönbein, a plant in the act of growth, by causing a reaction of the elements of air upon aqueous vapor, is a generator of nitrite (hyponitrite) of ammonia, and thus prepares a part of its own nitrogenous food. On this theory, the nitrogen of vegetables is derived indirectly from the constituents of the atmosphere. The quantity of nitrogen in an organic compound, may be determined either by separating the element in the gaseous state, or by converting it into ammonia, and precipitating this alkali by chloride of platinum. These methods will be presently described (p. 513).

Sulphur.—Sulphur is frequently associated with nitrogen. The nitrogenous principles of the animal and vegetable kingdom—albumen, fibrin, and casein—contain it abundantly. Gelatine and indigo contain nitrogen but no sulphur; gutta-percha contains a trace of sulphur but no nitrogen; while caoutchouc contains both. Sulphur is an important constituent of certain essential oils. In dried organic solids, it may be detected by heating the substance in a small tube: the vapor evolved, containing sulphuretted hydrogen, blackens a slip of glazed card, or of paper impregnated with a salt of lead. Dried gluten, bread, caoutchouc, flannel, hair, horn, or feathers, evolve a quantity of a sulphur compound under these circumstances. If the substance also contains nitrogen, ammonia is produced, and hydrosulphate of ammonia comes over with aqueous vapor. The detection of the hydrosulphate and therefore of the presence of nitrogen and sulphur, in the compound, is readily effected by one experiment. Paper wetted with a solution of nitro-prusside of sodium, acquires immediately a rich purple or crimson color. Unless the sulphur is in combination with an alkali, this change does not take place (p. 214).

There are other methods of detecting sulphur. The substance may be boiled in a solution of potassa containing a small quantity of oxide of lead dissolved (p. 199): if sulphur is present, the substance is either blackened or the liquid acquires a dark color from the production of sulphide of lead. A portion of flannel or silk thus tested by a potassa-solution of oxide of lead, will be completely blackened; but if mixed with cotton, the fibres of the latter will remain white, as this substance contains no sulphur. Liquid compounds of sulphur which are dissolved by potassa undergo a similar change (p. 273). As an alkaline sulphide is produced by the reaction of the potassa on the sulphur of the organic matter, the nitroprusside of sodium may be made available for the detection of this element. If a small quantity of hair, woollen, or silk is boiled in a solution of potassa, the presence of sulphur will be indicated by the alkaline liquid acquiring a reddish or crimson tint when a few drops of nitroprusside of sodium are added. For this purpose, potassa, free from lead, should be selected.

Owing to the frequent presence of lead as an impurity in solution of potassa, most sulphur-compounds, when boiled with the alkali, impart to it a dark color.

In some cases, the molecular condition of the substance interferes with the application of this test. Thus caoutchouc contains much sulphur, but in order to detect it, the substance should either be digested in strong nitric acid containing nitrous acid, or deflagrated in a silver crucible with pure hydrate of potassa and nitre, until it has become white. The sulphur is oxidized and converted into sulphuric acid or sulphate of potassa, and the quantity of acid produced may be determined by precipitating a neutralized solution of the residue in water, with baryta or one of its salts (p. 207).

Phosphorus.—This is not unfrequently associated with nitrogen and sulphur in organic compounds, and exists sometimes in large proportion in animal products. In the state of phosphoric acid combined with soda, lime, or magnesia, it is an abundant mineral constituent of animal and vegetable matter, and is readily obtained by incineration. Its presence and proportion may be determined, by deflagrating the dried organic substance with a mixture of equal parts of pure nitrate of potassa and bicarbonate of potassa in fine powder. The experiment may be performed in a platinum crucible: the saline residue is dissolved in water, and the solution neutralized with acetic acid. Any soluble phosphate that is present may be precipitated by the methods described at pages 235 and 361. In the first case ammonio-phosphate of magnesia is produced, 100 parts of which when dried and ignited, are equivalent to 28·57 parts of phosphorus (p. 340), and in the second an insoluble perphosphate of iron is thrown down.

The sulphur and phosphorus of the vegetable kingdom are chiefly derived from a deoxidation of the sulphates and phosphates contained in the soil.

Chlorine, Bromine, and Iodine.—In all natural compounds these elements are found associated with alkaline metals, and are readily separated by the process of incineration. Artificial compounds, containing them in such a form as to yield no precipitate on the addition of nitrate of silver, may be analyzed by passing the vapors through a combustion-tube containing a mixture of three parts of hydrate of lime and one part of hydrate of soda, the purity of which has been previously ascertained. A chloride, bromide, or iodide of the alkaline metal is thus procured. After the tube has cooled, the lime is dissolved in very diluted nitric acid; and nitrate of silver is added to the filtered solution. A precipitate, consisting of chloride, bromide, or iodide of silver, or a mixture of these salts, is thus obtained, and the proportion of each element may be determined by the process described at page 193. Volatile compounds of these elements are introduced into the mixture in small glass bulbs (*see* p. 513).

When the substance for analysis consists of carbon in combination with hydrogen or oxygen, or with both of these elements, the proportions in 100 parts may be at once determined by the use of the *Combustion-tube.*

The tubes used in these analyses, should be made of green glass free from lead, or of hard Bohemian glass, and are generally about four-tenths of an inch in diameter, and from 15 to 18 inches in length, sealed, and either drawn into a point or rounded at the sealed end; the open extremity should be smoothed by fusion, so as to receive a cork without danger of cracking. It is sometimes necessary to protect the tube, by rolling a strip of copper-foil spirally round it, tied at each end by a piece of wire. The tube may be heated, either by a lamp-furnace or over charcoal, in a trough of sheet-iron constructed for the purpose.

When the substance to be analyzed is solid, from 3 or 4 to 8 or 10 grains of it, properly dried, are carefully mixed with about 200 grains of the dried oxide of copper, and introduced into the combustion-tube, into the end of which is previously placed about half an inch in length of small copper-shavings superficially oxidized. These shavings should occupy about two inches of the tube above (or, as it lies horizontally, before) the organic mixture, the object being to keep the whole contents of the tube in a loose or porous condition, so that the gaseous products may escape from it without impediment. The mixture of oxide of copper and the organic substance should be placed about the centre of the combustion tube, some pure oxide of copper being placed before and behind it. If the organic substance under examination is a ternary compound of hydrogen, carbon, and oxygen, it is obvious that the products will be only *water* and *carbonic acid.* In order to ascertain the weight of the former, and thence the weight of the *hydrogen* required to form it, the products, as they escape, are carried through a tube containing fragments of fused chloride of calcium, and accurately weighed. The vapor of water is absorbed, and the increase in the *weight* of the tube and its contents, will indicate its quantity (p. 507). The juncture of the combustion-tube with the chloride of calcium tube, should be made air-tight by a perforated cork.

The carbonic acid, deprived of water, is conducted from the extremity of the chloride of calcium tube, into a light glass tube blown into five bulbular enlargements, containing a strong solution of caustic potassa, and accurately balanced. The bulb apparatus is then connected with the chloride of calcium tube, by short lengths of caoutchouc piping.

After the abstraction of the *water* in the chloride of calcium tube, the carbonic acid passes on into the solution of caustic potassa, through which, by properly inclining the bulb apparatus, it may be made to pass in divided bubbles, and under some pressure, so as to insure its total absorption. When the experiment is completed, the apparatus is allowed to cool, and in order to prevent any portion of the alkaline solution retrograding into the chloride tube, the tip of the combustion-tube is broken off, and any residuary carbonic acid may then be drawn into the alkaline solution, by applying gentle suction at the end, or by the use of an aspirator. The weight of the evolved carbonic acid, and therefore of the carbon, is ascertained by accurately determining the increase in the weight of the condenser with its alkaline solution (p. 507).

In order to illustrate the mode of operation, we may assume that 10 grains of pure starch have been thus decomposed by oxide of copper in the combustion-tube, and that the chloride of calcium tube has acquired an increase of weight equal to 5·94 grains (water), and the potassa apparatus has increased in weight 16·24 grains (carbonic acid). As pure starch is known to contain only carbon, hydrogen, and oxygen, the proportions of each element in 100 parts may be thus determined. Hydrogen forms one-ninth part of water: hence $5{\cdot}94 \div 9 = 0{\cdot}66$ H. In 22 parts, by weight, of carbonic acid, there are 6 parts of carbon : hence 22 : 6 : : 16·24 : 4·43 C. The oxygen, if these results are correct, may be determined by deducting the sum of the weights of hydrogen and carbon from the weight of the starch employed in the experiment, $0{\cdot}66 + 4{\cdot}43 = 5{\cdot}09$; and $10 - 5{\cdot}09 = 4{\cdot}91$ O. Hence these results show that pure starch consists of:—

	In 10 parts.	In 100 parts.
Carbon	4·43	44·3
Hydrogen	0·66	6·6
Oxygen	4·91	49·1
	10·00	100·0

When *nitrogen* is a constituent of the organic matter under examination, the mixture with oxide of copper is made as usual, but the contents of the fore part of the combustion-tube must now consist of a mixture of shavings or filings of metallic copper with the oxide, and great care must be taken slowly to conduct the evolved gases through this mixture, rather highly heated, in order to effect the complete evolution of the nitrogen, and to decompose the various compounds which that substance might possibly form with the oxygen, carbon, or hydrogen. The nitrogen then escapes as a gas with carbonic acid. The gases may be collected in a proper mercurial apparatus, and the carbonic acid removed afterwards by a few fragments of fused hydrate of potassa, when the nitrogen will remain, and its weight may then be deduced from its volume. Deutoxide of nitrogen is an occasional product of the decomposition of a nitrogenous compound by oxide of copper. It is most readily formed when chromate of lead, or a current of pure oxygen, is employed in the combustion-tube. It is produced in larger quantity, *cæteris* *paribus*, when the temperature is high, than when the combustion takes place slowly.

The quantitative determination of nitrogen may be more accurately obtained by converting it into *ammonia*, and in this form combining it with chloride of platinum, so as to weigh it in the state of ammonio-chloride. (VARRENTRAPP and WILL, *Ann. der Chem. und Pharm.*, 39, 257.) For this purpose the azotized organic product, to the amount of 4 or 5 grains, is thoroughly blended in a warm mortar with a mixture of 1 part of dry hydrate of soda, and 2 of lime, in such quantity as to fill the combustion-tube to within about 3 inches of its open end. Attached to the combustion-tube is a three-bulbed apparatus, containing pure hydrochloric acid, sp. gr. 1·130. Heat is then applied to the combustion-tube, beginning at the anterior extremity; and when the whole length has been so heated that the substance has become quite white, air is drawn through it as in the case where oxide of copper is used, and the contents of the bulb-apparatus poured into a basin, the bulbs being afterwards washed, first with a mixture of alcohol and ether, and then with water, from an ounce to an ounce and a half of liquid being used for that purpose. A solution of pure chloride of platinum is then added in excess to the mixture of the hydrochloric solution and washings, and the whole evaporated to dryness: the residue is treated with a mixture of two volumes of alcohol and 1 of ether; if this affords a yellow solution, excess of chloride of platinum has been added, and the remaining washed ammonio-chloride of platinum may be collected on a filter, dried at 212°, and weighed. In order to control the weighing, the ammonio-chloride should be calcined, and the resulting metallic platinum also weighed. 100 parts of the dried ammonio-chloride, are equivalent to 6·22 of nitrogen and 44 parts of metallic platinum. All substances containing nitrogen, under these circumstances, evolve this element in the form of ammonia, excepting nitric acid. If any soda-lime is carried over it does not affect the result, as these alkalies are not precipitated by chloride of platinum. Any excess of chloride of platinum is completely removed by the mixture of alcohol and ether.

The soda-lime, before use, should be ignited and finely powdered. In its reaction on organic matter at a high temperature, it is probable that the carbon unites with the oxygen of the water of the hydrates, forming carbonic acid, which unites to the bases, while the hydrogen which is set free combines with the nitrogen of the organic substance to produce ammonia. Three parts of hydrogen are sufficient for the entire conversion of fourteen parts of nitrogen. If the nitrogenous compound is a liquid, it may be introduced into bulbs and heated with soda-lime in the manner in which organic liquids are heated with black oxide of copper (*see* below). Some nitrogenous organic substances do not evolve ammonia under these circumstances, but a volatile organic base on which soda-lime has no action. Thus, indigo yields aniline, and other substances produce other bases containing no oxygen. They all form, however, insoluble compounds with chloride of platinum and the amount of nitrogen present admits of easy determination by incinerating the salt and obtaining the platinum in the metallic state. 99 parts of platinum are equivalent to 14 of nitrogen or 100 parts to 14·4.

If the substance for analysis is a volatile organic *liquid* (alcohol), it may be collected in a small balanced bulb of glass, and its weight accurately determined after sealing the capillary end of the bulb. It may then be dropped into the midst of the oxide of copper in the combustion-tube, the small capillary end being previously broken. After the oxide has become full heated in the fore-part of the tube, the portion containing the bulb is heated, and as the vapor of the liquid escapes, it is immediately decomposed by the ignited oxide of copper. Two of these bulbs, containing together from 6 to 8 grains of the liquid, may be employed in one operation, provided that several inches of the oxide are interposed between them. It the liquid has a high boiling-point and is rich in carbon, it will be found better to subdivide the quantity among three bulbs. Substances of a viscid or fatty nature may be introduced into the combustion-tube in small glass tubes, or in trays of platinum foil.

In the analysis of hydrocarbons, it is sometimes necessary to use a current of pure oxygen, in order to consume the carbon completely. Occasionally chlorate of potassa is mixed with oxide of copper, in order to insure a copious supply of oxygen. Chromate of lead, as a source of oxygen, has some advantages over oxide of copper. After it has been fused, it is but little hygrometric; and if the substance which is to be analyzed, contains chlorine or sulphur, the lead retains these elements, while with oxide of copper a volatile chloride of that metal is formed, as well as sulphurous acid. This last-mentioned compound is not absorbed by chloride of calcium, but it readily combines with potassa, and thus adds to the apparent amount of carbon. In order to avoid this source of error, a tube containing finely-powdered peroxide of lead, should be placed between the chloride of calcium tube, and the potassa-apparatus. This completely arrests any sulphurous acid that may be produced. With the use of chromate of lead, however, the tube containing peroxide is seldom required.

Sulphur can be estimated only by the process described at p. 510. Nitric acid is not always efficient in completely oxidizing the sulphur of organic compounds. Liebig advises that the substance should be gradually fused in a silver crucible with an excess of a mixture of 8 parts of hydrate of potassa and 1 part of nitre. If the mixture should not become colorless when heated, a little more nitre may be added. The white residue is dissolved in water acidulated with hydrochloric acid, and this solution is precipitated by chloride of barium. The sulphate, after it has been washed, dried, and ignited, may be weighed: 100 parts of dried sulphate of baryta are equivalent to 13·8 of sulphur. Volatile organic liquids containing sulphur may be vaporized, and the vapor passed through a tube containing a mixture of nitre and bicarbonate of potassa or soda, strongly heated.

[For further information on the analysis of organic substances, the reader is referred to Fresenius's *Quantitative Analysis*, p. 385, and Liebig's *Handbook of Organic Analysis.*]

EQUIVALENTS OF ORGANIC SUBSTANCES. FORMULÆ.=The results obtained by the use of the combustion-tube, merely represent the weights of the elements in 100 parts. There can be no doubt that these elements are combined in equivalent proportions, and the principles on which the atomic weight of an organic compound is calculated, are therefore similar to those described for mineral substances (p. 61). We may take for illustration an alkaloid, an acid, and one or more neutral substances.

1. An *Alkaloid.*—One hundred parts of morphia yield by combustion: of carbon, 71·91; of hydrogen, 6·85; of oxygen, 16·44; and of nitrogen, 4·80. The hydrochlorate of this base may be readily obtained anhydrous, and it is found that 100 grains of the anhydrous salt contain 88·75 of morphia and 11·25 of hydrochloric acid. Assuming this analysis to be correct, the atomic weight of the alkaloid will be 292 (11·25 : 88·75 : : 37 : 292). The weight of each element contained in this quantity of the alkaloid, is easily deduced from the elementary analysis of 100 parts. Thus—

$$\begin{array}{rcrcrcl} 100 & : & 71{\cdot}91 & :: & 292 & : & 209{\cdot}97 \text{ Carbon} \\ 100 & : & 6{\cdot}85 & :: & 292 & : & 20{\cdot}00 \text{ Hydrogen} \\ 100 & : & 16{\cdot}44 & :: & 292 & : & 48{\cdot}00 \text{ Oxygen} \\ 100 & : & 4{\cdot}80 & :: & 292 & : & 14{\cdot}01 \text{ Nitrogen} \end{array}$$

If the weight of each element, contained in an equivalent of morphia, is divided by its atomic weight, the products will represent the number of atoms contained in each atom of morphia:—

Parts.		Equiv.		Atoms.		Atoms.
209·97	÷	6	=	34·99	or	35 of Carbon
20·00	÷	1	=	20·00	or	20 of Hydrogen
48·00	÷	8	=	6·00	or	6 of Oxygen
14·01	÷	14	=	1·00	or	1 of Nitrogen

The formula for morphia is, therefore, $C_{35}H_{20}O_6N=292$. When it is required to calculate the percentage composition of the alkaloid from its formula, we adopt an inverse method. Thus:—

Atoms.		Equiv.		Parts.
35	×	6	=	210 Carbon
20	×	1	=	20 Hydrogen
6	×	8	=	48 Oxygen
1	×	14	=	14 Nitrogen
				292

and—

$$\begin{array}{rcrcrl} 292 & : & 210 & :: & 100 & 71{\cdot}91 \text{ Carbon} \\ 292 & : & 20 & :: & 100 & 6{\cdot}85 \text{ Hydrogen} \\ 292 & : & 48 & :: & 100 & 16{\cdot}44 \text{ Oxygen} \\ 292 & : & 14 & :: & 100 & 4{\cdot}80 \text{ Nitrogen} \end{array}$$

Alkaloids which form double chlorides by combining with chloride of platinum, may have their equivalents determined by a calculation based, 1st, on the weight of the platinum salt in the dry state, and 2dly, on the weight of the metallic platinum obtained as a result of its combustion.

2. An *Organic Acid.*—For the purpose of illustration, we may take Oxalic acid. This and other acids are first combined with oxide of silver or oxide of lead, taking care that the compounds are neither basic nor hydrated. The oxalate of lead, dried at 212°, consists of 24·32 of oxalic acid, and 75·68 of oxide of lead, or 36 parts of the acid are required to form a definite salt with 112 parts (or one equivalent) of oxide of lead. This acid contains no hydrogen, so that in burning the dry lead-salt with well-dried oxide of copper, no water is formed, and the only product is carbonic acid: 100 grains of Oxalic acid, ($\bar{O}$), are thus found to contain 33·33 parts of carbon and 66·67 of oxygen: and $11{\cdot}99 \div 6 = 1{\cdot}99$, or 2C, and $24 \div 8 = 3O$: hence anhydrous oxalic acid is represented by C_2O_3: and from this formula, its centesimal composition may be deduced as in the case of morphia.

$$\begin{array}{rcrcrcl} \bar{O} & & & & \bar{O} & & \\ 100 & : & 33{\cdot}33 & :: & 36 & : & 11{\cdot}99 \text{ Carbon} \\ 100 & : & 66{\cdot}67 & :: & 36 & : & 24{\cdot}00 \text{ Oxygen} \end{array}$$

Alkaloids and acids which either crystallize, or form crystallizable salts, frequently combine with water to form hydrates. To avoid error in this respect, it is sometimes advisable to ascertain the atomic weight of an alkaloid by determining, by precipitation, the proportion of acid (sulphuric or hydrochloric) contained in a weighed quantity of the crystallized salts. In reference to crystallizable acids, the amount of water combined with the crystals of Oxalic acid may be thus determined: 63 grains of the acid dissolved in water, and precipitated by acetate of lead, yield 148 grains of dry oxalate of lead. Deducting the weight of the oxide (148—112=36), we obtain the weight of dry acid which has combined with the lead. As 63 grains of crystallized acid were used in the experiment, then 63—36=27, or three equivalents of water must have been combined with them. Hence crystallized Oxalic acid has the formula $C_2O_3,3HO$, or, as it cannot exist without an atom of water, $C_2C_3,HO+2HO$.

3. *Neutral Bodies.*—In reference to neutral substances which do not enter into combination with mineral compounds of which the equivalents are known, there are great difficulties in assigning a correct atomic constitution. In some cases they combine with oxide of lead, and from this combination, a formula may be deduced: gum, sugar, and starch are bodies of this kind: on the other hand, some, such as mannite, enter into no known combination. The general rule regarding organic substances of this nature, is to divide the quantity of each element contained in 100 parts, by its equivalent. The quotients thus show the relations which the elements bear to each other in atoms or equivalents, and if fractional, these may be converted into integers by multiplication.

Cane-sugar may be combined with oxide of lead; and, by analysis, it is found that this compound contains in 100 parts, 59·3 of oxide of lead and 40·7 of sugar. If an atom of sugar were united to an atom of oxide of lead, then the equivalents would be 76·87 for (59·3 : 40·7 : : 112 : 76·87), but there is great reason to believe that 2 atoms of oxide of lead replace 2 atoms of water which are contained in crystallized sugar; and therefore that the equivalent of anhydrous sugar is 153; (76·87×2=153·74). One hundred parts of crystallized cane-sugar give by combustion:—

								Atoms.
Carbon .	41·50	÷	6	=	6·92	1·064	=	11·7 or 12
Hydrogen	6·45	÷	1	=	6·45	0·993	=	10·9 or 11
Oxygen .	52·05	÷	8	=	6·50	1·000	=	11·0 or 11

The figures in the fourth column are obtained by making oxygen the unit and divisor,—thus, 69·2÷6·50=1·064; 6·45÷6·50=0·993; and 6·50÷6·50 =1. The quotients multiplied by 11 give the results in atoms at 11·7, 10·9, and 11 respectively, or, in round numbers, $C_{12}H_{11}O_{11}$. Deducting the 2 atoms of water which are known to exist in crystallized cane-sugar, the formula would stand thus: $C_{12}H_9O_9+2HO$. When sugar combines with oxide of lead, the two atoms of water are replaced by two of this oxide, so that saccharide of lead would be $C_{12}H_9O_9,2PbO$, or 153 parts of sugar (1 atom) to 224 parts of oxide of lead (2 atoms). The formula here given is well adapted to explain the conversion of sugar into alcohol, as well as various other chemical changes of this compound. If, from the formula of crystallized cane-sugar ($C_{12}H_{11}O_{11}$), we desire to calculate the centesimal composition, so as to compare the theoretical with the ascertained results, the differences will be no greater than might be explained by slight errors in analysis. This will be evident from the following figures:—

	Atoms.						Calculated.	Found.
Carbon . .	12	×	6	=	72	or	42·11	41·50
Hydrogen . .	11	×	1	=	11	or	6·43	6·45
Oxygen . .	11	×	8	=	88	or	51·46	52·05

Mannite is a compound of three elements. In 100 parts it consists of:—

Carbon .	39·54	÷	6	=	6·59	1·00	×	6	=	6
Hydrogen	7·73	÷	1	=	7·73	1·17	×	6	=	7
Oxygen .	52·73	÷	8	=	6·59	1·00	×	6	=	6

The atoms of carbon, hydrogen, and oxygen, as deduced from the centesimal composition, are as the respective numbers, 659, 773, 659. If the figures in the third column are divided by the amount of oxygen as unity, quotients are obtained which, when multiplied by 6, give a series of atoms in integers, namely, $C_6H_7O_6$. These figures, therefore, merely express the proportions of the elements in reference to their atomic weights. They convey a better knowledge of the composition of bodies than the arithmetical proportions in 100 parts; and are so far convenient for use. At the same time formulæ thus derived, are purely *empirical.*

Volatile Liquids.—When the organic compound is a volatile liquid, its *vapor-density* will serve to control the results of an analysis. In the series of isomeric liquid hydrocarbons, it is chiefly by the vapor-density of each liquid, that the number of atoms which should enter into the respective formulæ, can be accurately determined. The degree of condensation of the elements is therefore a material point in considering their atomic constitution, and in constructing their formulæ. 100 parts of *Alcohol* yield by the combustion-tube:—

				Atoms.
Carbon . .	52·65 ÷ 6	= 8·92	8·92 ÷ 4·30	= 2
Hydrogen .	12·90 ÷ 1	= 12·90	12·90 ÷ 4·30	= 3
Oxygen . .	34·45 ÷ 8	= 4·30	4·30 ÷ 4·30	= 1

The sp. gr. of the vapor of alcohol is 1·61: hence, if this analysis be correct, the specific gravities of the elements in these atomic proportions should correspond. With respect to carbon, the volume of its vapor, compared with hydrogen, cannot be determined experimentally. It is assumed that one volume or atom is represented by the sp. gr. 0·4146. Oxygen has a sp. gr. of 1·1057, and hydrogen a sp. gr. of 0·0691, hence:—

	Atoms.	Sp. gr.	
Carbon . . .	2	(0·4146 × 2)	= 0·8292
Hydrogen . . .	3	(0·0691 × 3)	= 0·2073
Oxygen . . .	1	(1·1057 ÷ 2)	= 0·5528
Sum of specific gravity . . .			1·5893

The sp. gr. of the vapor of alcohol is therefore nearly in accordance with that which should be found in one volume of a vapor of which the constituents are 2 atoms (or volumes) of carbon, 3 atoms (or volumes) of hydrogen, and 1 atom (or half a volume) of oxygen. The most simple formula for alcohol would therefore be C_2H_3O. Alcohol has neither acid nor basic properties, and forms no definite compounds with bodies. Hence its equivalent might be taken at twice, three times, or even four times the numbers of the atoms above given. The theory of the production of sulphovinic acid and of ether by the reaction of sulphuric acid on alcohol, is rendered much more simple by doubling the numbers obtained by analysis, and making them $C_4H_6O_2$. In this case the atom of alcohol would correspond to *two volumes* of its vapor; and its specific gravity compared with air would be as 1·61 to 1·00, and with hydrogen as 23 to 1. The conversion of alcohol into aldehyde and acetic acid by processes of oxidation, is rendered more intelligible by the adoption of the formula above given.

Rectified *Oil of turpentine* yields by analysis in 100 parts:—

			Atoms.
Carbon	88·24 ÷ 6	= 14·70	1·25 or 5
Hydrogen	11·76 ÷ 1	= 11·76	1· or 4

Its formula as thus deduced, would be, in its most simple form, 5 atoms of carbon and 4 of hydrogen (C_5H_4). But it might also be $C_{10}H_8$ or $C_{20}H_{16}$. The ascertained specific gravity of the vapor compared with air is 4·76. A constitution represented by C_5H_4 would give for the specific gravity, only one-half of this density, or 2·35. $C_{10}H_8$ would give a density of 4·70, resembling so closely that which has been determined by experiment, that it is impossible not to conclude that 10 atoms of carbon and 8 atoms or volumes of hydrogen are included in each *volume* of the vapor of oil of turpentine. The oil, however, combines with some of the hydracids, including the hydrochloric. With the latter it forms a solid artificial camphor, represented by $C_{20}H_{16},HCl$. The formula for the oil of turpentine should be, therefore, $C_{20}H_{16}$, unless it be supposed that 2 atoms of the oil $2(C_{10}H_8)$ are combined with 1 of hydrochloric acid. The former is selected by reason of its greater simplicity and its agreement with the formulæ of other hydrocarbons. One atom of oil of turpentine, like one atom of alcohol, therefore corresponds to *two volumes* of vapor: hence the specific gravity would be about 4·7 :—

	Atoms.		Vol.					
Carbon	20	or	20	=	0·4146	×	20	8·292
Hydrogen . . .	16	or	16	=	0·0691	×	16	1·105
	1		2					9·397
Vapor-density of oil of turpentine								4·698

Chloroform is considered to have the constitution represented by the formula C_2H,Cl_3. The specific gravity of its vapor is 4·20. This is in accordance with the view, that each atom of the compound corresponds to *two volumes* of the vapor :—

	Atoms.		Vol.		Sp. gr.			Sp. gr.
Carbon . . .	2	......	2	=	0·4146	×	2	0·8292
Hydrogen . .	1	......	1	=	0·0691	×	1	0·0691
Chlorine . .	3	......	3	=	2·4876	×	3	7·4628
	1		2					8·3611
Vapor-density of chloroform . . .								4·1805

As a general rule the vapor-density shows the proportions in which the elements combine, but the atomic weight can be correctly determined only by calculation from some definite compound. In the case of chloroform no such compound is known. This and other instances prove that in the vapors of organic liquids, the gaseous elements undergo an enormous condensation.

When the formula of an organic substance merely expresses the number of atoms of each element, as $C_4H_6O_2$ (alcohol), or $C_4H_4O_4$ (hydrated acetic acid), it is called *empirical.* It expresses the relative proportions of the elements, without reference to the mode in which they are combined, or to the atomic weight of a body. A *rational* formula implies one which professes, upon certain hypotheses, to define the mode of union or actual arrangement of atoms in a compound, of which the equivalent has been determined by experiment.

We here necessarily enter into a region of speculation. Thus, out of an atom of alcohol a variety of rational formulæ may be constructed, according to the hypothesis which a chemist may adopt. The empirical formula of alcohol ($C_4H_6O_2$) may be expressed by C_4H_5O+HO, or $2C_2H_2+2HO$, or $2CO+2CH_2,+H_2$. The empirical formula of hydrated acetic acid ($C_4H_4O_4$) may, according to the radical theory, be converted into the rational formulæ ($C_4H_3O_3+HO$, or $2(C_2H_2)+O_4$).

Compound Radicals.—In inorganic chemistry, radicals are represented by simple substances which enter into combination with oxygen, chlorine, and other electro-negative bodies. Sulphur (S) is the radical of sulphuric acid (SO_3), and sodium (Na) is the radical of chloride of sodium (NaCl). In order to assimilate organic to inorganic chemistry, it has been suggested that some of the atoms of organic substances may be so arranged as to form compound radicals, which are assumed to combine with the electro-negative elements, O, Cl, and S, to form binary compounds, like those met with in inorganic chemistry. Cyanogen is a well marked instance of a compound radical. It is represented by the formula C_2N (p. 260) and it acts in all respects like an element. It combines with hydrogen and all the metals like an electro-negative body, and with oxygen and chlorine like an electro-positive body. A compound radical, therefore, is simply a body which combines, like an element, with other elementary bodies. It may also enter into combination with other compound radicals. In the cyanide of cacodyle (KdCy, or $C_4H_6As+C_2N$) we have an instance of two compound radicals combining like elements.

Organic radicals, a few of which have been isolated, while the greater number have only an hypothetical existence, may consist of two, three, or more elements. When they contain carbon and hydrogen only, they generally terminate in *yle*, and are represented by a symbol, like elements. Thus, the radical of alcohol (C_4H_5) is called *Ethyle*, and is represented by the symbol Ae. Ether would therefore be an oxide of ethyle (C_4H_5,O, or AeO). *Formyle* (C_2H) (Fo) is the radical of formic acid, and this acid is C_2H,O_3, oxide of formyle, or FoO_3. *Methyle* (Me) is C_2H_3; *Acetyle* (Ac) C_4H_3. *Cacodyle*, which consists of carbon, hydrogen, and arsenic, is C_4H_6As, and has the symbol Kd. This view of the constitution of organic compounds has been generally adopted. While it is open to some objections, there can be no doubt that it has greatly facilitated the study and classification of organic substances.

Substitutions.—As in mineral chemistry, one negative element may be substituted for another, HO becoming HCl by the substitution of chlorine for oxygen, so in reference to organic radicals, a smilar change may be observed. Formic acid is converted into chloroform by the substitution of three atoms of chlorine for three atoms of oxygen, the radical remaining the same: thus C_2H+O_3 becomes C_2H+Cl_3; and whole series of compounds may be thus constructed, in which one negative element simply replaces another negative element, according to the usual laws of equivalent proportions. There is, however, another remarkable character in organic compounds, to which the term *substitution* is specially applied—namely, where the electro-negative may take the place of an electro-positive body, the compound remaining unaltered in its type; *i.e.* the elements being otherwise in the same number, proportion, and, as it is supposed, molecular arrangement, differing in fact only in equivalent weight. Hydrated acetic acid ($C_4H_3O_3,HO$) may have its hydrogen replaced by chlorine, to form chloracetic acid ($C_4Cl_3O_3,HO$), the electro-negative chlorine being substituted for the electro-positive hydrogen. A similar substitution is observed in the conversion of chloride of methyle into chloroform by chlorine: $C_2H_3Cl+4Cl=C_2H,Cl_3+2HCl$.

In the production of pyroxyline from cellulose (p. 560), a certain number of atoms of nitrous acid (NO_4) are substituted for an equal number of atoms of hydrogen, the other constituents remaining unchanged. Benzole ($C_{12}H_6$) is in like manner converted by nitric acid into nitro-benzole ($C_{12}H_5[NO_4]$), by the removal of an atom of hydrogen, and the substitution of an atom of nitrous acid, as in the following equation:—

$$\underbrace{C_{12}H_5H}_{\text{Benzole.}} + \underbrace{NO_5}_{\text{Nitric acid.}} = \underbrace{C_{12}H_5(NO_4)}_{\text{Nitrobenzole.}} + \underbrace{HO}_{\text{Water.}}$$

Water is a product of this reaction: and, when we compare the chemical and physical properties of benzole with those of nitrobenzole, there is probably no more remarkable change in organic chemistry, than that which this substitution effects.

Nitrobenzole admits of a still further change, by a removal of its oxygen, and the addition of two atoms of hydrogen: it is thereby transformed into *Aniline*, and becomes the source of an extensive series of most valuable dyes:—

$$\underbrace{C_{12}H_5(NO_4)}_{\text{Nitrobenzole.}} + \underbrace{2HO}_{\text{Water.}} + \underbrace{4Fe}_{\text{Iron.}} = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + \underbrace{2Fe_2O_3}_{\substack{\text{Sesquioxide} \\ \text{of iron.}}}$$

By simple distillation with water and metallic iron, this remarkable metamorphosis is brought about; and by assuming that aniline contains an atom of the compound radical, *Phenyle* ($C_{12}H_5$), this base is frequently described as a compound ammonia, in which one atom of phenyle is substituted for one atom of hydrogen. Thus ammonia being NH_3, aniline ($C_{12}H_7N$) may have its atoms thus arranged on the type of ammonia ($C_{12}H_5$) NH_2. It is questionable how far the application of the names of well-known chemical substances, possessed of entirely different properties, to compounds of this nature, is beneficial to science. It rests entirely on assumption; for the atomic arrangement of the elements is insusceptible of proof; and although the doctrine of substitutions affords some ground for the view, it tends to produce in the mind of a student a confusion of hypothesis with fact. The term *ammonia* is in these cases employed in an entirely new sense: it is intended to signify, not the well-known gaseous compound of nitrogen and hydrogen, of defined properties and composition, but a substance wholly different, and having only an hypothetical resemblance to it in chemical constitution. Thus, a body which contains one atom of nitrogen, associated with one or more atoms of hydrogen, and a group of atoms which is supposed to replace the deficient hydrogen, is designated an "*ammonia.*" This may be better illustrated by the following table, in which the composition of ammonia is given, and the atomic constitution of the radical, substituted for the hydrogen, is also represented. It should be observed that Phenyle ($C_{12}H_5$) has only an hypothetical existence, while Methyle (C_2H_3) and Ethyle (C_4H_5) have been isolated.

		Radical substitute for 1 atom of hydrogen.		
Ammonia . . .	N H H H ……			
Methylamine . .	N H H Me ……	Me	=	C_2H_3
Ethylamine . .	N H H Ae ……	Ae	=	C_4H_5
Diethylamine . .	N H Ae Ae ……	2Ae	=	C_8H_{10}
Triethylamine . .	N Ae Ae Ae ……	3Ae	=	$C_{12}H_{15}$
Aniline . . .	N H H Ph ……	Ph	=	$C_{12}H_5$

These are all considered to be ammonias, or substitution-compounds of ammonia. They agree in constitution, in having 1 atom of nitrogen, associated with 3 atoms of hydrogen, or with 1, 2, or 3 atoms of the compound radical. In accordance with this hypothesis it has been proposed to call aniline *Phenylamine;* but there appears to be no good reason for changing a universally received name upon purely hypothetical grounds. Ammonia itself might, with an equal disregard of custom and utility, be called *Nitramine,* just as arsenuretted and antimonuretted hydrogen have been recently designated Arsenamine and Stibamine. The latter are described as "ammonias" of arsenic and antimony, because they happen to be constituted of one atom of a metallic radical (replacing nitrogen), and three atoms of hydrogen. The terms *alcohol*, *aldehyde*, *ether*, *urea*, &c., hitherto restricted to well-known special bodies, have been thus vaguely applied by some chemists to compounds presenting certain hypothetical resemblances of constitution. As nothing is really known of the atomic constitution of compounds, such a system of nomenclature, if recognized, must necessarily lead to perpetual changes, and to endless confusion. Aniline has already borne the names of Kyanol, Phenylamide, Phenylia, and Benzidam. Its present designation points to its original source from indigo. It involves no hypothesis of constitution, and is therefore not liable to be changed by the progress of discovery. While there can be no objection to any new organic compound being designated according to the fancy of its discoverer, there is a serious objection to the application of old and well-known names to new substances, or to the use of such names in a sense entirely different from that in which they have been hitherto universally accepted.

CHAPTER XLV.

PROXIMATE ORGANIC PRINCIPLES. STARCH. GUM. PECTOSE. GELOSE. SUGAR.

THE proximate principles of the vegetable and animal kingdoms often bear a close resemblance to each other. Thus sugar, oil, albumen, and coloring matter, are found in both. Gum appears to be of purely vegetable origin, but starch, which has been hitherto considered to be vegetable, has been found, according to some authorities, in a modified condition in the organs of animals. Urea is peculiar to the animal kingdom. In this and the following chapters we shall group together those substances which possess analogous properties, whether of vegetable or animal origin.

STARCH ($C_{12}H_{10}O_{10}$).—Starch (*Fecula. Amylum*) is an organized substance, abundant in the cellular tissue of certain parts of plants: it is usually seen in the form of a white and somewhat glistening powder, of a specific gravity of about 1·5, which, when pressed, produces a peculiar crackling sound, and feels somewhat elastic. Under the microscope it is seen to consist of small spheroidal grains, differing in size and shape; the largest, and those best adapted to microscopical examination, are obtained from the rhizome of the *Canna coccinea*, known under the name of *Tous les Mois:* they are about one-260th of an inch diameter; they appear wrinkled, and as if made up of concentric layers, and a fissure (*hilum*) may generally be observed upon some part of the grains, which has been regarded as the spot where they adhered to the cell containing them. Examined by polarized light, these granules present a black cross, the centre of which appears to correspond with the hilum. In wheat-starch this cross is not easily observed, but in potato-starch it is distinct, so that it has been resorted to as a means of detecting the adulteration of wheat-starch with the cheaper varieties.

Starch is generally represented as insoluble in cold water; and indeed the usual mode of obtaining it, which consists in diffusing the rasped or ground vegetable in cold water, and washing and collecting the deposit, seems to justify such conclusion; but if potato-starch is triturated with water at 60°, and the mixture poured upon a filter, the filtrate contains starch: and if a dilute solution of starch in hot water is cooled to 60° and filtered, there is starch in the filtered liquor. But as starch is an organized substance, and cannot be obtained in that state of purity which belongs to crystallized products, and, as it is convertible into gum and sugar, it may be doubted how far some of the properties ascribed to starch, actually belong to this body in its pure form.

Starch is rapidly disintegrated by hot water: when 1 part of it is gradually heated in 15 parts of water to about 130°, it begins to change its appearance, and at 140° or 150° the whole acquires a pasty consistence, and the microscope shows that in this state the granules are swollen and broken: if the paste is diffused through water a large portion of them subsides, and the supernatant fluid retains some starch, in a modified state, in solution. If starch-paste be subjected, under pressure, to a temperature of about 300°, a solution is obtained which, on cooling, deposits minute spherical granules of about one-4000th of an inch diameter, and having the leading chemical characters of the original starch; so that in this way the varieties of starch may be brought to the same physical condition.—(JACQUELAIN.)

Starch is insoluble in alcohol and in ether. It forms a tenacious paste with weak solutions of potassa or soda, but not with ammonia. With iodine it forms a characteristic blue compound, which, provided the iodine is not in excess, loses color when heated to about 160°, but regains it on cooling; it is also decolored, with the production of hydriodic acid, by exposure to light. This property renders iodine a valuable test for starch, and starch for iodine. Paper imbued with a mixed solution of starch and iodide of potassium is immediately blued by free chlorine and bromine, and has been used as a test for ozone (p. 105).

The ultimate elements of pure wheat-starch, dried at 212°, are represented as $C_{12}H_{10}O_{10}$, but when in combination with oxide of lead the compound appears to be $C_{12}H_9O_9,PbO$, so that the more correct formula for starch is C_{12},H_9,O_9+HO; but starch, in its ordinary state, retains a larger proportion of water, and it varies in the different varieties of starch. When 1 part of starch is dissolved in 150 of boiling water, and precipitated by ammoniacal acetate of lead, the composition of the precipitate is $C_{12}H_9O_9+2PbO$. Starch, when gelatinized by weak solutions of potassa or of soda, may be thrown down from these alkaline liquors by neutralizing them with acetic acid, and then adding alcohol. A cold solution of starch is also precipitated by tannic acid, or infusion of galls.

The principal commercial varieties of starch are, 1. Wheat-starch; 2. Potato-starch; 3. Rice-starch; 4. Arrowroot-starch, obtained from the tubers of the *Maranta arundinacea;* 5. Sago, from the stems of certain palms, and which is usually granulated; 6. Tapioca, the starch of the *Jatropha manihot;* 7. Tous les Mois, from the rhizome of the *Canna coccinea;* 8. Otaheite arrowroot, from *Canna pinnatifida;* 9. Portland arrowroot, from the tubers of *Arum maculatum.*

Metamorphoses of Starch.—When starch is carefully heated to about 300° it becomes soluble in cold water, is no longer rendered blue by iodine, and has acquired many of the leading properties of gum: the term *Dextrine* has been applied to this substance from its turning the plane of polarization to the *right* when acting on polarized light. But there are other means of effecting this change of starch into dextrine (and ultimately into *sugar*), amongst which the most remarkable is that produced by a peculiar azotized principle called *diastase* (from διΐστημι, to separate), and which is formed in germinating seeds and growing buds. It occasions the change of the amylaceous part of the seed into gum and sugar, during a certain period of its growth; and it is in consequence of its presence in *malt* that the brewers' *sweet worts* are produced, and that the addition of a little malt to unmalted grain changes a large proportion of its starch into saccharine or fermentable matter.

Diastase may be obtained from carefully prepared malt, by bruising and digesting it in water at 70° to 80°: the pasty mixture is then pressed, and the liquor which runs from it filtered, heated to about 170°, and again filtered: this filtrate retains the diastase, and may be used for many purposes as a solution of that substance, but it also retains other matters which may be separated by absolute alcohol: this throws down the diastase. It is a white flocculent substance, soluble in water, insoluble in alcohol, tasteless, and easily decomposed: its effects upon starch are destroyed at a boiling heat: its ultimate composition has not been determined, but as certain other organic products effect similar changes upon starch, such as gastric juice, animal membrane, yeast, &c., its claims to be considered a distinct principle have been doubted. Its power of changing starch into dextrine and sugar is such that 1 part of it is capable of thus modifying 2000 parts of starch: its effect may be well shown by adding a little of it to a thick starch paste, heated to about 180°; it immediately becomes fluid, gummy, and sweet.

When starch-paste is warmed with water acidulated by sulphuric acid, it also passes into dextrine. The same change may be effected by very dilute nitric acid: Payen's method consists in moistening 10 parts of starch with 3 of water, containing one-150th part of nitric acid, and drying it in thin layers in a stove heated to about 240°. In two hours the conversion is complete.

Dextrine ($C_{12}H_{10}O_{10}$) is nearly tasteless, uncrystallizable, soluble in water, insoluble in alcohol, and of the same composition as starch and gum; it is not blued but reddened by iodine, and differs from gum in forming a deep blue liquor with a solution of sulphate of copper, which deposits suboxide of copper when boiled. With acetate of lead and ammonia it gives a precipitate $=C_{12}H_{10}O_{10},2PbO$.

Uses of Starch.—Starch is not only largely consumed in the manufacture of dextrine, but is in common use for stiffening various fabrics and articles of wearing apparel; and for this purpose a slight blue tinge is generally given by a little indigo, Prussian blue, or smalt. Thin and cheap calicoes are often largely imbued with starch and sulphate of soda, to make them appear of greater substance than they really are.

Lozenges, and various articles of confectionery, consist partly of starch. Cheap sugar-plums are composed of refuse starch, with chalk, gypsum, and other trash: a spurious *refined liquorice* is also made upon the same principle. *Stone-blue* is a compound of indigo, or Prussian blue, and the inferior kinds of starch. Among the substances used to adulterate starch, porcelain-clay was at one time prevalent. Considered as an article of food, as a part of the diet of children and of invalids, and as a component of our most nutritious vegetables, starch is very important. But, although eminently adapted to form part of our food, it is not fitted for exclusive nutriment; and this is the case with all vegetables deficient in nitrogen.

GUM ($C_{12}H_{11}O_{11}$).

Several modifications of a distinct proximate principle of vegetables are included under the term *gum:* they are not organized, like starch, nor are they crystallizable, like sugar: they either readily dissolve in water, hot or cold, or swell up into a viscid mass when moistened; and they are tasteless, and insoluble in alcohol and in ether. Their principal varieties may be described as *Arabine* and *Bassorine.*

Arabine, as represented by Gum Arabic, is the produce of various species of *Acacia;* its sp. gr. is from 1·30 to 1·50. It forms a viscid mucilage with water, which slightly reddens litmus, and leaves a transparent glaze or varnish when it dries. Alcohol throws down a white hydrated gum from its solution: it produces a rotation to the left of a polarized ray of light. The alkalies and alkaline earths form soluble compounds with arabine, but with several metallic oxides (*e.g.* lead and iron) it produces definite, insoluble precipitates, which have been called *Arabinates:* thus, with subacetate of lead the white compound which falls is $PbO,C_{12}H_{11}O_{11}$. It is not precipitated by a solution of neutral acetate of lead, but it is thrown down by persulphate of iron and nitrate of mercury. When potassa is added to a solution of gum and sulphate of copper, a blue arabinate falls, which is not decomposed by boiling: this distinguishes arabine from dextrine. Many of the concentrated acids decompose gum, but when boiled with very dilute sulphuric acid it is gradually changed into dextrine and glucose. It absorbs chlorine and produces a peculiar acid: it also absorbs hydrochloric acid. Nitric acid converts it into *Mucic acid* ($C_{12}H_8O_{14}2HO$.) Bromine and iodine are without action upon it. Oxalate of ammonia indicates the presence of lime in a solution of gum arabic, and lime is found in its ash.

Bassorine. Tragacanthine.—Gum Tragacanth may be taken as the type of this modification of gum. It is the produce of different species of *Astragalus.* When steeped in water it swells into a bulky mucilaginous mass, which, when long boiled, acquires the general properties of arabine. Cherry-tree gum, or *Cerasine,* and the gum which exudes from peach and apricot trees, and other species of *prunus,* seems to be a mixture of arabine and bassorine. There is also a number of mucilaginous substances, such as those derived from quince-seed, linseed, marshmallow root, &c., which closely resemble the varieties of gum.

PECTOSE. *Vegetable Jelly.*—A gelatinous principle has long been recognized as one of the proximate components of vegetables: it is derived, according to Frémy, from the presence of *Pectose* (*πηκτὸς, coagulated*), a substance usually associated with the cellular tissue, and which is insoluble in water, alcohol, and ether, but which, under the influence of acids, aided by a gentle heat, becomes converted into a soluble gelatinous substance, *Pectine,* represented by the formula $C_{61}H_{48},O_{64}$. Pectine is found ready formed in the juices of ripe fruits, in consequence of the action of their acids upon the original *pectose.* It may be obtained from the expressed juice of ripe pears or apples (after the lime which it contains has been precipitated by oxalic acid, and the albumen by a strong solution of tannin), by means of alcohol, which throws it down in gelatinous filaments. When pure, it is white, neutral, not crystallizable, soluble in water, but insoluble in alcohol and in ether: it is precipitated by subacetate, but not by neutral acetate of lead. When its aqueous solution is long boiled, it loses viscosity, and is changed into *parapectine,* which does precipitate neutral acetate of lead; and if boiled with a dilute acid, it is further modified into *metapectine,* which is distinguished by precipitating a solution of chloride of barium.

Pectic Acid ($C_{32}H_{20}O_{28},2HO$).—Pectine and its modifications are changed into *pectic acid* by the action of weak alkaline solutions; and the soluble *pectates* thus formed may be decomposed by other acids. Pectic acid is generally obtained by boiling the pulp of certain roots, of carrots, for instance, with a very weak solution of an alkaline carbonate, and precipitating by chloride of calcium; the precipitate, after having been well washed, is decomposed by dilute hydrochloric acid, which leaves the pectic acid in the form of a jelly, insoluble in cold water, but which, when long boiled in water, is changed into *parapeptic acid,* which is soluble in water, sour, and is precipitated from its solutions by baryta water: its formula is ($C_{24}H_{15}O_{21},2HO$). Under the influence of powerful acids, or alkaline bases, pectine and its modifications are further changed into *metapectic acid,* ($C_8H_5O_7,2HO$), which forms soluble salts with all bases.

Pectic Fermentation.—Pectose is always associated with a substance which Frémy calls *Pectase,* having a special action upon it (as diastase has upon starch), and which he represents as the *ferment* of the gelatinous products.

It is obtained by adding to fresh carrot-juice, alcohol, which throws it down in an insoluble form, but it retains its characteristic properties. It transforms pectine (at a temperature between 80° and 90°) into a substance insoluble in cold water (*Pectosic acid*), and subsequently into Pectic acid, as above described. None of these pectic compounds exert any rotatory action on polarized light.

GELOSE.—There are many Algæ, Fuci, and Lichens, which abound in a peculiar gelatinizing principle. One of the most remarkable is the *Gelidium corneum*, from which an article is prepared known commercially as *Japan Isinglass.* The gelidium corneum contains 58 per cent. of substances soluble in boiling water. The dried gelatinous compound obtained from it is insoluble in cold, but soluble in hot water. It sets into a firm jelly on cooling, even when it forms only one-120th part of the weight of the water. One part of isinglass (animal gelatin) produces a similar jelly with about 80 parts of water. The vegetable jelly is neutral, tasteless, and imputrescible. It is insoluble in alcohol, ether, and weak acids. Unlike animal jelly, it is not precipitated in solution by tannic acid, and it is not altered by a solution of iodine or subacetate of lead. It has been proposed to substitute it for the varieties of animal gelatine, but it is destitute of nitrogen, having the formula $C_{24}H_{21}O_{24}$ (*Rep. de Pharm.*, Jan. 1860). The edible birds'-nests, esteemed as a delicacy in China, are constructed by a species of swallow, of the *Plocaria candida.* In some of these Algæ, however, Dr. Davy has found from 2 to 4 per cent. of nitrogen ; and it is probable that researches directed to the use of these allied vegetables as food, would greatly extend the number of edible species. Many of them abound also in a modification of sugar (*Mannite*) and they are extensively used as manures and as sources of iodine.

The *Chondrus crispus* (Irish, or Carrageen moss) contains nearly 80 per cent. of a gelatinous principle which has been called *Carrageenin* ($C_{12}H_{10}O_{10}$) ; and in the *Cetraria Islandica* Berzelius found from 40 to 50 per cent. of a mucilaginous matter which he compares to starch. (*See* " Stanford on the Economic applications of Seaweed," *Journ. Soc. of Arts*, Feb. 1862.)

SUGAR.

There are two leading varieties of sugar. CANE-SUGAR (*Sucrose*) and GRAPE-SUGAR (*Glucose*). To these some writers have added FRUIT-SUGAR, or *Fructose.*

CANE-SUGAR ($C_{12}H_9O_9,2HO$) is chiefly obtained from the sugar-cane, each gallon of its juice yielding about a pound : it is also derived from beetroot, which yields from 4 to 5 per cent. ; from the sap of the sweet maple, and from some other sources, especially from the stalks of Indian corn or maize, the juice of which is nearly as rich in sugar as that of the cane. Several of the palm tribe, such as the date and cocoa-palm, are also important sources of this kind of sugar.

The general characters of cane-sugar, and its ordinary commercial varieties are well known. Its sp. gr. is about 1·6 ; it dissolves in one-third its weight of water at 60°, producing a viscid *syrup*, which affords, by spontaneous evaporation, prismatic crystals of *candy.* A solution saturated at 230°, concretes into a granular mass or tablet; but when boiled down until it acquires a tendency to vitreous fracture on cooling, or till a portion thrown off from a stirrer, concretes, or *feathers* as it falls, it congeals into a transparent amorphous mass (*barley-sugar*) which, however, has a tendency to become opaque, and pass into a granular crystalline texture, exhibiting a case of dimorphism : this change is prevented by the addition of a little vinegar or tartaric acid. Absolute alcohol dissolves about one-80th of its weight of this sugar at its boiling-point, nearly the whole of which separates in small crystals on cooling. If equal parts of strong syrup and of alcohol are mixed, a quantity of small brilliant crystals of sugar is soon deposited. Pure cane-syrup is not prone to change; but certain substances, when present only in very minute proportions, materially affect the stability of the solution, and lead to a series of curious changes which will be adverted to under the head of *Fermentation.*

When a thin cane-syrup is long-boiled, it gradually grows less viscid, and slowly passing into a modified state, ultimately becomes brown and uncrystallizible; so that, where saccharine liquids are concerned, the protracted application of heat should be avoided; and if mere traces of acid or alkali be present, these changes are promoted, and new products result, some of which form insoluble compounds with the majority of basic bodies, and have been termed *melassic* and *melassinic acids;* others resemble ulmic and humid acid (*sachulmine*).

Refining of Sugar.—The process of *refining* sugar, or of converting the varieties of raw, brown, or Muscovado, into white loaf-sugar, is extensively carried on in London and Liverpool. The sugar is first dissolved in lime-water, by the aid of steam, in a metal tank called the *blowing-up* pan, and a portion of bullock's blood, technically termed *spice*, is usually added, the albumen of which, as it coagulates, entangles many impurities, carrying them to the surface, and so enabling them to be skimmed off, together with some insoluble products of the action of the lime. The liquor, thus far clarified, is then transferred to a series of cotton filtering bags, till it runs through them quite bright, but still of a dark color. To decolor it, it is passed through bone-black, or other varieties of charcoal, contained in vertical metallic cylinders, the effect of which is to render the dark-colored syrup colorless and bright. In this condition, and of proper strength, it is transferred into the *vacuum pan*, and boiled down under diminished pressure, and at a temperature of about 150°, till of sufficient density to be drawn off into a vessel now termed the *heater*, but which when, as formerly, the syrup was boiled down over an open fire, and at a temperature of not less than 230°, was called the *cooler.* Here the temperature of the syrup, now inclined to crystallize, is raised to about 175°, under constant stirring, and it becomes a kind of magma, which is *filled out* into proper conical moulds of copper, zinced iron, or earthenware, the orifice at the apex of each mould being plugged by a paper stopper. As soon as this magma has consolidated upon the upper surface (or the base of the cone) it is well stirred up again, and in due time the stoppers are removed, so as to allow the uncrystallized liquid to drain away into vessels placed for its reception. The loaves are now submitted to a peculiar washing or cleansing operation, sometimes called *claying*, which consists in the application of a thick mortar or magma of sugar and water (now used instead of clay) to the base of the loaf, portions of the fluid from which gradually percolate the loaf, carrying the dark-colored syrup, or treacle, before them. Finally, an operation termed *liquoring* is resorted to; that is, a dense and very pure syrup is poured upon the base of the loaf, previously smoothed by a *bottoming trowel*, and as this filters through the cone, it deposits a portion of its sugar in its way, and at the same time washes out the relics of colored syrup. When this process is completed, and all percolation has ceased, the loaf is knocked out of the mould, and if above 16 pounds' weight, is truncated by cutting off the apex, so as to form what is called a *lump*, or *titler;* or if intended for a *loaf proper*, a new apex is given to it by a conical cutter or *nosing machine.* Finally, the loaves are *papered*, and deposited on trellised shelves in a room called the *stove*, heated to about 130°, till dry throughout.

GRAPE-SUGAR; *Glucose* ($C_{12}H_{14}O_{14}$, or $C_{12}H_{12}O_{12}+2HO$).—This modification of sugar abounds in grapes, figs, plums, and other fruits: it is also the result of the action of *diastase*, and of dilute acids upon starch. In good seasons the expressed juice of grapes yields from 30 to 40 *per cent.* of solid matter, the greater part of which is this kind of sugar. When obtained from fruits, it is accompanied by more or less of an uncrystallizable sugar (*Fruit-sugar* or *Fructose*, $C_{12}H_{12}O_{12}$), which, however, by assimilating the elements of water, passes into the condition of grape-sugar, or glucose. The conversion of starch into this kind of sugar has been adverted to (p. 522). It is a process extensively carried on as a commercial manufacture, especially in France. Potato-starch and sago are principally used: they are saccharized by the action of dilute sulphuric acid (10 parts of acid to 1000 of water and 500 of starch). The dilute acid is heated by steam, and the starch, previously mixed with water of a temperature between 112° and 130°, is suffered gradually to dribble-in under constant stirring; its conversion into dextrine is immediate: in about two hours and a half the whole of the starch is added, and in from 15 to 25 minutes afterwards, the saccharification is complete; the steam is then shut off, and the liquor transferred to another vat, in which the acid is saturated with chalk. When the sulphate of lime has subsided, the clear liquid is drawn off and evaporated to the sp. gr. of about 1·26. The resulting syrup is then left to deposit the sulphate of lime separated during evaporation, and afterwards drawn off perfectly clear. In this state it may be used as a source of alcohol, or for sweetening colored liquors; but it requires, for the greater number of purposes, to be deprived of color, which is done by filtering it through animal charcoal. When required in its solid state, the syrup is evaporated in a steam vat till of a sp. gr. of about 1·4, and then poured into coolers, where it concretes.

Glucose, or fruit-sugar, differs from sucrose, or cane-sugar, in being less soluble in water, and more soluble in alcohol, so that the two may be to some extent separated by the action of alcohol. The sweetening power of glucose is also greatly inferior to that of sucrose, 2 parts of the latter being in this respect equivalent to about 5 of the former. Sucrose easily crystallizes in prisms, but glucose forms tubercular concretions, or fibrous acicular groups, $= C_{12}H_{12}O_{12},2HO$. Both these sugars form definite crystallizable compounds with chloride of sodium.

When cane-sugar is heated to about 320° it melts, and at about 400° becomes brown, deliquescent, and slightly bitter, losing water (2 atoms), and passing into *Caramel*, $= C_{12}H_9O_9$. In this state it is used for coloring wines and spirits: it is soluble in water, but is thrown down from its solution by excess of alcohol. It combines with certain bases, such as baryta and oxide of lead, forming insoluble compounds. Heated to about 500°, melted sugar bursts into flame, and leaves a porous mass of nearly pure charcoal.

When grape-sugar is heated to 212° it softens, and loses 2 atoms of water becoming ($C_{12}H_{12}O_{12}$); at 284° it passes by further loss of water into caramel, $C_{12}H_9O_9$, and at a higher temperature is entirely decomposed.

Solutions of cane and of grape-sugar produce a right-handed rotation upon a ray of polarized light.

Concentrated sulphuric acid acts energetically upon cane-sugar, evolving water, carbonic and formic acids, and charcoal. It is a striking experiment to mix about equal bulks of oil of vitriol and strong syrup: the mixture, when stirred, becomes brown and black, then suddenly heats, boils up, and passes into the state of a bulky black magma: the acid appears suddenly to abstract the elements of water from the sugar, leaving charcoal.

The action of sulphuric acid upon grape-sugar is very different: it merely renders it brown, and a new compound, *sulphosaccharic acid*, is produced, characterized by forming soluble salts with lime and baryta.

Boiled with very dilute sulphuric or hydrochloric acid, cane-sugar becomes fruit or grape-sugar, by the assimilation of an atom of water; and under the influence of yeast (*see* ALCOHOLIC FERMENTATION) there is a similar transition of the one species of sugar into the other; but the converse change, namely, that of grape or fruit-sugar into cane-sugar (glucose into sucrose), cannot be effected. Nitric acid changes the varieties of sugar into saccharic and oxalic acids. In the presence of decomposing casein and chalk, sugar forms *lactic acid*, and under the influence of certain substances occasionally present in raw sugar, it passes into a ropy mucilage and into mannite.

Action of bases upon Sugar.—When lime or baryta is boiled with sugar and water a bitter solution is formed, which is said to contain a definite *saccharide* ($2CaO$, or $2BaO, + C_{12}H_9O_9$). Freshly precipitated oxide of lead is similarly dissolved, and on cooling, a white compound falls, which, after having been dried at 212°, is $= 2PbO + C_{12}H_9O_9$. Many of these compounds are soluble in excess of alkalies, and hence the presence of sugar sometimes prevents the precipitation of metallic oxides from their salts. In other cases sugar tends to reduce the oxides. The compounds of *glucose* with bases are less stable than the preceding, this sugar gradually passing in *glucic acid* ($C_{12}H_5O_5, 3HO$), which under the influence of heat becomes *apoglucic acid* ($C_{18}H_9O_8, 2HO$): and ultimately *melassic acid* is formed. Grape-sugar is distinguished from cane-sugar by boiling it in a solution of potassa. The former alone darkens as the result of the formation of glucic acid. This is commonly known as Moore's test.

Tests for Sugar.—The deoxidizing property of glucose above-mentioned is the foundation of a valuable test of its presence; and inasmuch as the other varieties of sugar are transformed into glucose by the joint action of very dilute acids and heat, the same mode of testing is applicable to sugar generally. Certain salts of copper and of platinum are especially applicable to these purposes. When a little cane-sugar is added to a dilute solution of copper, and the mixture heated, little immediate change ensues; but with fruit-sugar the blue color of the liquor is presently changed to green, it then becomes yellowish or reddish-brown, and suboxide of copper or metallic copper falls: these changes are more rapid when a little alkali has been added to the solution. The best form of the copper-test of the presence of sugar is the *soda tartrate of copper*, obtained by dissolving recently precipitated tartrate of copper in a solution of soda or of carbonate of soda: it is immediately discolored, and reduced; when boiled with a trace of glucose; and when used quantitatively, it will be found that 15 parts of the precipitated suboxide of copper are equivalent to about 5 of *cane-sugar*. A hot solution of nitrate of suboxide of mercury is immediately blackened by glucose, and finely divided mercury falls: in the same way a boiling solution of corrosive sublimate deposits calomel, which is afterwards partially reduced: red oxide of mercury is also reduced when boiled in the saccharine solution. Solutions of nitrate of silver and of chloride of gold, when boiled with glucose, afford precipitates of silver and gold: when in these cases, excess of carbonate of soda is present, the effect is more rapid, and in this way the chlorides of platinum and palladium are reduced. A delicate test of glucose is the soda-chloride of platinum formed by adding excess of a solution of carbonate of soda to a moderately dilute solution of chloride of platinum.

When this solution is boiling, an atom of cane-sugar dropped into it produces no effect, but it is instantly discolored, and ultimately blackened, by the smallest trace of fruit-sugar. Where these tests are used, the absence of other organic matters likely to effect their decomposition, must be insured.

The ultimate components of the preceding varieties of sugar are as follows:—

SUCROSE.			GLUCOSE.		
Atoms.	Equiv.	Per cent.	Atoms.	Equiv.	Per cent.
C 12 ...	72 ...	42·11	C 12 ...	72 ...	36·36
H 11 ...	11 ...	6·43	H 14 ...	14 ...	7·08
O 11 ...	88 ...	51·46	O 14 ...	112 ...	56·56
1·	171	100·0	1·	198	100·00

Honey.—The substance secreted in the nectaries of flowers is converted by the bee into honey and wax: the portion not required for their food, is returned into the combs in the form of a yellow syrup, the qualities of which differ according to the flowers whence it has been derived. In its original liquid state it probably resembles uncrystallizable sugar of fruits, &c. (Fructose, $C_{12}H_{12}O_{12}$); but when kept for some time, a large portion of it passes into a granular form, identical with glucose $=C_{12}H_{14}O_{14}$. But honey also contains a little wax, gum, coloring matter, and mannite.

Diabetic Sugar, or that which is formed in a diseased state of the animal system (*diabetes*), has all the properties of grape-sugar or glucose. It may be separated from the extract of diabetic urine by boiling alcohol.

Mannite; Manna-Sugar ($C_6H_7O_6$).—This substance is most abundant in manna, but also found in beetroot, celery, asparagus, onions, and probably in other sweet plants: it is also contained in the sap of the *larch*, and other species of *pinus* (*Manna Brigantina*). It has been detected by Dr. Stenhouse in *Laminaria Saccharina*, and some other fuci. Manna exudes from several species of *ash*, especially from the *Fraxinus ornus* and *rotundifolia. Mannite* is obtained by boiling manna in alcohol, from which it crystallizes in acicular prisms. It forms about four-fifths of the best manna; the residue being chiefly common sugar, and a peculiar extractive matter, in which the aperient quality of the manna is said to reside. Mannite is also an occasional product of viscous fermentation.

Mannite is very soluble in water, but is not susceptible of vinous fermentation, so that it may in this way be separated from the other varieties of sugar; for, when mixed with them, it remains undecomposed in that process. Nitric acid converts it into saccharic and oxalic acids, without any trace of mucic acid. Its aqueous solution precipitates basic acetate of lead, forming a compound in which 2 equivalents of water are replaced by two of oxide of lead, $=C_6H_5O_4,2PbO$. It reduces chloride of gold and nitrate of silver, but does not precipitate an alkaline solution of tartrate of copper. It combines with sulphuric acid, forming *sulphomannitic acid*, $=C_6H_5O_4,2SO_3$.

Glycyrrhizine ($C_{35}H_{32}O_{12}$) is the sweet principle of *liquorice-root:* it forms difficultly soluble compounds with many acids and bases, and is not susceptible of vinous fermentation.

There are some other substances allied to these modifications of sugar, which do not require detailed notice, such as *Melitose* and *Eucalyn*, the produce of the *Eucalyptus mannifera; Sorbine*, from the berries of the mountain-ash; *Quercite*, from acorns.

CHAPTER XLVI.

ALCOHOLIC OR VINOUS FERMENTATION. ALCOHOLIC LIQUIDS.

By fermentation, we are to understand the conversion of an organic substance into one or more new compounds, in presence of a body called a ferment (p. 500). Hence there are various kinds of fermentation, designated according to their products—vinous or alcoholic, lactic, butyric, acetous, &c. In vinous fermentation sugar is resolved into alcohol and carbonic acid. *Sugar* itself is not absolutely necessary to the process; for starch, dextrine, or any substance capable of being easily converted into sugar, under the circumstances, may be substituted, and similar products obtained. The conversion of the substance into sugar appears to be, however, an essential preliminary condition for the establishment of the process. It is well known that a portion of malt or saccharized barley, mixed with unmalted grain, will produce alcohol—the starch and dextrine of the unmalted grain being converted into sugar during the process. In the same way alcohol may be produced in large quantity, by the mixture of the starchy pulp of the potato with a portion of treacle. The fermentation of dough in the making of *bread* appears to depend on similar principles; a portion of the starch is converted into sugar, and in the presence of a ferment, the sugar is immediately resolved into alcohol and carbonic acid.

Pure sugar, extracted from the vegetable and dissolved in water, has no tendency to undergo this remarkable change. A solution of pure cane-sugar is slowly converted into grape-sugar, but there the change stops: no alcohol is produced. The saccharine juices of vegetables, however, readily ferment, owing to the presence of a nitrogenous principle with which they are usually associated. This is called a *ferment.* It is an organic compound containing nitrogen, and is readily susceptible of change by simple exposure to air. In this state it possesses the property of rapidly inducing changes in any saccharine liquid. Gay-Lussac observed long since, that when fresh grape-juice was collected in a vessel containing carbonic acid, and placed over mercury, no fermentation took place, although all other circumstances were favorable to this process. When the juice was exposed to air and a proper temperature, it rapidly fermented, and when once this fermentation had commenced, it continued until the saccharine matter was entirely decomposed. If to the unfermented juice, placed over mercury, a few bubbles of air or oxygen were admitted, the same change took place, and continued until the sugar was exhausted, a large quantity of carbonic acid being at the same time evolved, while the liquid was found to have lost its saccharine, and to have acquired a spirituous or alcoholic flavor. These facts prove that there is present in grape-juice, a substance which by contact with oxygen undergoes a change, and becomes a ferment; and further, that the saccharine juices of fruits do not ferment, because the access of free oxygen is cut off by the epidermis of the fruit.

A saccharine solution of malt, called *wort*, will undergo similar changes, by reason of the nitrogenous principles contained in the grain. The custom is, however, to add to the liquid, for the purpose of accelerating the change, a quantity of nitrogenous compound called *yeast*, or *barm*, derived from a previous fermentation. This constitutes the ferment. It produces a rapid conversion of the saccharine matter into alcohol and carbonic acid; and at the same time causes the separation of the nitrogenous principles of the wort in the form of additional ferment or yeast. The quantity of new yeast thus procured, amounts to seven or eight times the quantity of that which has been added to the wort.

It has been shown by Mitscherlich (*Poggend. Ann.*, iv. 224), that the actual contact of the particles of the yeast with the dissolved sugar is essential. He suspended a wide glass tube, the bottom of which was closed with bibulous paper, in a jar of a solution of sugar, the tube being itself filled with the same solution. Some yeast was then put into the syrup contained in the tube, where it soon induced fermentation, and the alcohol there formed, passed through the pervious bottom, and, together with carbonic acid, diffused itself in the surrounding liquor: but the actual phenomena of fermentation—namely, the decomposition of the sugar and the formation of alcohol and of carbonic acid—were limited to the syrup in the tube containing the ferment, and the sugar in the outer vessel remained unchanged. Quevenne found that yeast which had been deprived of all matter soluble in water, still retained its power of exciting fermentation. The active part of yeast is composed of minute vesicles, or globules, and during fermentation these germinate in the saccharine liquor, producing a microscopic fungus, the *Torula* or *Mycoderma cerevisiæ*. The plant, according to one theory of the process, is supposed to grow at the expense of the sugar, giving out carbonic acid, and leaving alcohol. According to Andral and Gavarret (*Ann. Ch. et Ph.*, 3ème sér., viii. 399), there are two species of vegetable seeds contained in yeast, which may be separated by diluting it with water: in a few days globules fall to the bottom of the vessel, forming a gray pulverulent deposit which is extremely active in producing alcoholic fermentation when added to saccharine solutions; but at the same time a film forms upon the surface of the liquid, which consists of germs (of *Penicillum glaucum*) having no power to excite fermentation: these latter germs make their appearance in all acid albuminous liquids, and become *filamentous*, while the true producer of alcoholic fermentation always retains its *globular* form. According to Mitscherlich, the active part of yeast which remains after it has been washed with water, consists of:

	Before fermentation.		After fermentation.
Carbon	47·0	……	47·6
Hydrogen	6·6	……	7·2
Nitrogen	10·0	……	5·
Oxygen	35·8	……	
Sulphur	0·6	……	

Of this yeast (in the dry state) from 2 to 3 parts are required for the decomposition of 100 parts of sugar; and if there is excess of sugar, it remains unchanged after the fermentation. That portion of the yeast which remains in the form of a deposit after fermentation is over, is inefficient as a ferment; it appears, when examined under the microscope, to consist of the ruptured cells, and is not susceptible of vegetation; so that during the fermentation of sugar, a certain portion of the yeast-plant dies, and is decomposed, the living plant being required to sustain the fermentative process. If more yeast be present than is required for the decomposition of a certain quantity of sugar, the deposit which is in that case formed, consists partly of broken and partly of entire cells, and the latter retain their power of inducing fermentation. It further appears that that portion of the yeast which has become inert as a ferment, has lost the greater part, if not the whole, of its nitrogen; and certainly, one of the results of the changes which ensue during saccharine fermentation, appears to be the formation of ammonia, which may, although so small in quantity as generally to elude observation, be easily detected amongst the gaseous products.

For the formation of artificial yeast or ferment, the requisites appear to be the presence of sugar, of an azotized principle, water, and exposure to air at a moderate temperature. Any nitrogenous substance partly decomposed may act as a ferment. Thus gluten, albumen, casein, or fibrin, of the vegetable or animal kingdom, provided it be in a state of change or partial decomposition, may act as a ferment to saccharine liquids.

To obtain a ferment, in the first instance, a quantity of ground malt may be made into a thick paste by the addition of some concentrated wort, at a temperature of about 70° to 75°, so as to convert the starch into sugar; a little alcohol is then added, and after a few days, when the violence of the fermentation has subsided, a deposit of ferment is formed. An *artificial yeast* may be thus prepared: A small handful of ordinary wheat flour is made into a thick paste with cold water, covered with paper, and left seven days in a warm room, being occasionally stirred (FOWNES).

The yeast-cells, when treated with an aqueous solution of iodine, are found to consist of a colorless envelope, of the nature of cellulose, containing a fluid which acquires a brown color from the iodine. If yeast is dried *in vacuo*, or at a low temperature, it is converted into a hard, horny, translucent substance. It reacquires its property of exciting fermentation when digested for some time in cold water. *German yeast* appears to be a partially dried mass of cells. It has undergone washing to free it from the impurities of the fermented liquid, and is then dried at a low temperature. This yeast is chiefly obtained from the distilleries of Holland, and is now largely imported into England. Boiling water destroys the fermenting properties of yeast; but unless boiled so long as to have its chemical nature entirely changed, it reacquires a fermenting power on exposure to air. As the yeast-cells are composed of a cellulose envelope, containing an albuminous liquid, these properties are destroyed by chemical reagents: thus alcohol, common salt, strong acids and alkalies, destroy its fermenting power. Weak vegetable acids appear to accelerate fermentation. Yeast is generally acid, and this state of acidity probably operates favorably by converting any cane-sugar present in the fermenting liquid, into grape or fruit-sugar, which more easily undergoes fermentation.

The temperature which is found to be most favorable for vinous fermentation is about 70°, but it will take place at all temperatures between 40° and 80°. The lower the temperature the slower the process. At a high temperature the alcoholic rapidly passes into the acetous fermentation.

The process of vinous fermentation appears to be so identified with sugar, that it has been employed as a test for this principle; and the amount of carbonic acid obtained has been employed as a measurer of the quantity of sugar present. A strong solution of sugar will not, however, ferment; it requires a certain state of dilution with water, in order that the process should take place. Further, sugars differ among each other in the readiness with which they take on this property. Pure cane-sugar (*sucrose*, $C_{12}H_{11}O_{11}$) does not readily ferment; grape-sugar (*glucose*, $C_{12}H_{14}O_{14}$) is easily fermented, but the process takes place most readily in fruit-sugar (*fructose*), represented by $C_{12}H_{12}O_{12}$. The examination of the solutions of these sugars by polarized light, during fermentation, renders it highly probable that both cane and grape-sugar are converted into fruit-sugar before they undergo the change. These two sugars belong to the crystallizable variety, and their aqueous solutions are dextrogyrate under polarized light—*i. e.*, they turn the polarized ray from left to right. The fruit-sugar, which is uncrystallizable, is lævogyrate, turning the ray from right to left. Cane-sugar ferments slowly, because some time elapses before it is perfectly converted into fruit-sugar by the acids contained in the ferment. In this stage its rotatory power on polarized light is inverted. Cane-sugar also requires for its conversion, a much larger quantity of ferment than other sugars. When fermentation is complete, 100 parts of fruit-sugar are resolved into 51·12 of alcohol and 48·88 of carbonic acid, so that the ferment adds nothing to and removes nothing from the elements of sugar. In fact, it appears, by a catalytic action, simply to resolve the sugar into these two compounds. The changes may be thus expressed :—

$$\underbrace{C_{12}H_{11}O_{11}}_{\text{Cane-sugar.}} + \underbrace{HO}_{\text{Water.}} = \underbrace{C_{13}H_{12}O_{12}}_{\text{Fruit-sugar.}}$$

$$\underbrace{C_{12}H_{14}O_{14}}_{\text{Grape-sugar.}} = \underbrace{C_{12}H_{12}O_{12}}_{\text{Fruit-sugar.}} + \underbrace{2\,HO}_{\text{Water.}}$$

An atom of cane-sugar combines with the elements of water to produce fruit-sugar, while an atom of grape-sugar, by losing two atoms of water, becomes at once converted into fruit-sugar. 1 atom of this compound is resolved by fermentation into 4 atoms of carbonic acid, and 2 atoms of alcohol :—

$$\underbrace{C_{12}H_{12}O_{12}}_{\text{Fruit-sugar.}} = \underbrace{4\,CO_2}_{\text{Carbonic acid.}} + \underbrace{2\,C_4H_6O_2}_{\text{Alcohol.}}$$

How does the ferment operate to effect this remarkable change? Vital, chemical, and dynamical theories have been suggested, in order to explain the phenomena. The vital theory assigns the cause to the growth of a fungus derived from the yeast-cells. This is said to become developed at the expense of the sugar; but the objection to this view is, that the elements of the sugar are not removed by the fungus: they merely assume a new arrangement. Since the discovery of the fact that the ferment practically takes no direct share in the changes, no chemical theory has been suggested, which can adequately explain this conversion. The dynamical theory, advocated by Liebig, involves the assumption that the molecules of the ferment are in a state of motion, arising from their partial decomposition; and that this motion is mechanically communicated to the atoms of sugar, which thenceforth arrange themselves in the form of more stable compounds. This hypothesis, however, fails to explain why the particular compounds in question are invariably produced, or how the motion of atoms (if it exists) can bring about such remarkable chemical changes.

The phenomena of fermentation may be experimentally demonstrated by dissolving in a quart of water at a temperature of 70°, half a pound of treacle and half a pound of brown sugar, adding to the solution one pound and a half of bruised raisins, and a pint of fresh yeast. This mixture may be placed in a capacious glass globe, provided with a cork, and exposed to a temperature of from 70° to 80°. In about an hour fermentation will commence: the liquid will appear to be in continual motion, by reason of the bubbles of carbonic acid, as they are evolved, rising to the surface, and carrying with them portions of the yeast and the husks of the raisins. The gas there escapes, and as the solids again sink they gradually acquire a fresh coating of bubbles, which they carry up as before; and in this way that motion of the whole mass of liquor is produced which is so characteristic of active fermentation, and which, provided a sufficiency of ferment be present is maintained so long as any sugar remains to be decomposed. The process is attended by a considerable elevation of temperature, and when complete, the liquor clears, the yeast falls to the bottom, the sugar has vanished, and is replaced by alcohol. A trace of ammonia also at the same time makes its appearance.

Air or oxygen is not necessary to these changes: they go on readily in a close vessel. Too free an exposure of the liquid to air would cause a loss of alcohol, or the conversion of a part of this product into acetic acid. Although the ferment takes no direct part in the changes, a portion of it, equivalent to about 2 per cent. of the weight of the sugar, invariably disappears during the process. There is a certain relation between the proportions of sugar and ferment, which must be observed, in order to obtain the most satisfactory results. Regnault found that 4 parts of cane-sugar dissolved in 16 parts of water, required for their complete fermentation 1 part of fresh yeast. If the proportion of yeast is too small, it is decomposed before the entire conversion of the sugar, a portion of which remains unchanged in the liquid. If, on the other hand, the yeast is in too large a quantity, the sugar is entirely decomposed, and the residuary ferment afterwards undergoes the usual spontaneous changes. If more sugar be added, this will be converted into alcohol and carbonic acid until the ferment is exhausted. If in any case the sugar is in too large a proportion, the process is less active: and in a saturated solution of sugar, fermentation is altogether arrested. It was formerly believed that the ferment itself was not decomposed, but experiment has shown that there is invariably a consumption of it, although this is small in proportion to the sugar which is decomposed by it.

The properties of the products thus obtained from sugar may be easily demonstrated. If a lighted paper is introduced into the globular vessel when fermentation is complete, it will be extinguished: if a portion of the gaseous contents of the vessel is poured into a jar containing lime-water, and the vessel agitated, the liquid will become white from the production of carbonate of lime. If the gas is poured from the globe into another jar containing a solution of chloride of lime colored blue by litmus, the color will be destroyed on agitation, thus showing the presence of a gaseous acid. If during fermentation the aperture of the vessel is made air-tight, and connected by a bent glass tube with a jar full of water, and inverted over a water-bath, the carbonic acid may be collected as it issues in bubbles. The quantity which escapes is very large: it amounts to nearly half the weight of the sugar, 180 parts of fruit-sugar are converted into 92 parts of alcohol, and 88 of carbonic acid. Three drachms of fruit-sugar, when completely fermented, yield 187 cubic inches of this gas. One grain of fruit-sugar thus produces rather more than a cubic inch. In order to produce these quantities of alcohol and carbonic acid, there are required of grape-sugar 198 parts, and of cane-sugar 171 parts.

When the sugar is derived from malted grains, the liquid product of fermentation is called *beer;* when from the juice of the grape, it is called *wine.*

BEER.—This liquid consists chiefly of water and alcohol, with sugar, dextrine, coloring matter, essential oil, carbonic acid, and saline matters. Hops impart to it, as a result of the volatile oil and other principles contained in them, an aromatic bitter flavor, and an agreeable odor. They also diminish the tendency to subsequent fermentation. The color of beer depends on the temperature to which the malt has been exposed. Pale malt, *i. e.* malt which has not been exposed to a temperature above 140°, is in the best condition for the production of beer; but more color and flavor are imparted by malt which has been dried at a higher temperature. To a good beer brewed from pale malt, any depth of tint may be imparted by a careful use of roasted malt. Caramel or burnt sugar is sometimes employed as a coloring substance. The average amount of absolute alcohol, by measure, in the varieties of ale, is from 6 to 9 per cent.; less than six in common ale; in porter about 5 per cent.; and in small beer 1 to 2 per cent. Some of the stronger ales contain as much as 9 per cent. The method of determining the proportion will be described hereafter (*see* p. 536).

WINE.—The grape-sugar, or glucose, contained in the ripe grape, the juice of which is called *must*, is the source of the alcohol of wine. Besides water and alcohol, the fermented juice contains sugar, gum, coloring matter, malic and tannic acids, the bitartrate of potassa, tartrate of lime, and other salts, as well as volatile oil and œnanthic ether. Red wines contain much red coloring matter, which is derived chiefly from the red husks of the grapes. The husks also impart tannic acid, which gives astringency to port and similar red wines. The pale yellow or brown color of white wines arises from the fermentation of the juice only, or from fermentation over nearly colorless husks. The deep brown color of some wines (Tent wine) is more commonly produced artificially by the addition of caramelized grape-sugar. The dark-colored varieties of sherry frequently owe their tint to burnt sugar, or caramel.

All wines have an acid reaction, arising from the presence of the acid tartrate of potassa or lime, as well as of acetic acid, derived from a partial oxidation of the alcohol after the vinous fermentation is completed. In sparkling wines the acidity is partly due to carbonic acid. Malic acid is frequently present; and sulphuric acid, derived from the sulphuring of the juice to arrest fermentation, is also a cause of acidity. This may be found in comparatively large proportion in most sherry wines.

The amount of acid in wines may be determined volumetrically by the use of a standard diluted solution of ammonia, and a graduated burette. Some portion of the acid is volatile, and may be separated by distillation.

In all wines there is more or less of an odorous principle, partly derived directly from the grape, and partly formed during fermentation; it has the characters of an essential oil; it constitutes the *perfume* or *bouquet* of the wine, and in some wines is evanescent and small in quantity, in others more persistent and abundant. It does not exceed the forty-thousandth part of the wine. This odorous substance, which is formed in the process of fermentation, is represented by Pelouze and Liebig (*Ann. Ch. et Ph.*, liii. 115, and lxii. 439) as a true ether, that is, as a combination of oxide of ethyle with œnanthic acid. The formula $C_{14}H_{13}O_2$ is represented as that of œnanthic acid, which $+ C_4H_5O$ gives $C_{18}H_{18}O_3$ as the composition of *œnanthic ether*. Deleschamps first separated this ether from the wines of Burgundy, and it was afterwards recognized, together with amylic alcohol (potato-spirit oil), in the products of the distillation of the grapestalks of Montpellier.

Œnanthic ether (from οἶνος, *wine*), which is considered to be identical with pelargonic ether, may be obtained by agitating the oil derived from brandy or from grain-spirit (Weinfuselöl), which is a mixture of œnanthic acid and œnanthic ether, with a solution of carbonate of soda, till the free acid is neutralized; heat is then applied, and the œnanthic ether separates upon the surface, and may be dehydrated by chloride of calcium.

According to some, this ether exists ready formed in unfermented grape-juice. It is a colorless oily liquid, of a strong vinous odor, sp. gr. 0.862, boiling at 440°, soluble in alcohol and ether, but insoluble in water. A small quantity, however, passes over with the vapor of water during distillation. It has a strong taste and odor, as well as intoxicating properties. It imparts a powerful aroma, which is very persistent in any bottle or vessel that has contained wine: the odor is soon perceived over a very large apartment. Butyric, caprylic, acetic, and other ethers, are sometimes associated in wine with the œnanthic. The bouquet or perfume of wine is much affected by age. In some wines there is a fixed non-nitrogenous principle which has been called *œnanthin.*

During fermentation the bitartrate of potassa becomes less soluble, by reason of the production of alcohol; and the acidity of the wine, if dependent on the presence of this salt, diminishes, while its strength increases. This is deposited in the cask or bottle, either colored or colorless, according to the nature of the wine. It is well known under the name of crude tartar, or *argol.* Some wines which contain much sugar are observed, after a certain period, to become viscid or ropy. This has been called the *viscous fermentation.* It appears to arise from a spontaneous conversion of grape-sugar into an isomeric mucilaginous or gummy compound. Mannite is said to be a product, and hydrogen is evolved under these circumstances. Wines which contain much tannic acid are not liable to this change; and this acid, when added to wine thus affected, precipitates the mucilaginous compound. We have observed this change to take place in ale, arising probably from an excess of sugar and a deficiency of tannic acid in the hops.

Wines which are bottled before alcoholic fermentation is completed undergo this process still further; the carbonic acid accumulates in the liquid, and gives to the wine a sparkling character. An albuminous compound in the husk of the grape serves as a natural ferment to the juice. If the fruit-sugar is in excess, the wine will remain sweet after fermentation (Liqueur wines). If the ferment is in excess, the whole of the sugar will be decomposed and the wine will be slightly acid (Rhenish wines). If the sugar and ferment are equal, the wine is neither acid nor sweet (Burgundy.) (*Mulder on Wine,* 139.) When the sugar and ferment are thus equally balanced, the sugar almost entirely disappears, and a *dry* wine is the result. If, during fermentation, the alcohol reaches about 20 per cent. of the wine, the process is arrested, and any undecomposed sugar remains. In some of the Rhenish wines Fischern found the sugar so completely removed that, while it amounted to 21·7 per cent. of the grape-juice, it constituted only 0·1 per cent. of the wine (Liebfrauenmilch), the alcohol amounting to 9·9 per cent. and the dry extract to 4·1.

The *quantity of alcohol* contained in different wines is variable: the best mode of determining it consists in carefully distilling four ounces of the wine, until from one-half to three-fourths have passed over, having previously neutralized the acid of the wine by a little soda, potassa, or lime. A quantity of distilled water is then added to the portion of the alcoholic liquid which has gone over, so as accurately to make up the original volume of the wine: the mixture is well shaken and set aside for a day or two in a stoppered bottle, so that it may obtain its maximum density. Its specific gravity may then be taken in the usual way at 60°, and from this datum the proportion of alcohol may be determined by reference to tables which show the quantity of absolute alcohol contained in diluted alcohol of different densities (*see* p. 542). There is, of course, no direct relation between the original density of the wine and its alcoholic contents, inasmuch as some of the most alcoholic wines are also those which have the highest specific gravity, in consequence of the sugar, extract, and other substances which they hold in solution. Thus we have found some very strong wines to have a greater sp. gr. than water, the solid contents of the wine being in larger proportion.

Another method consists in gently distilling the wine until one-half is obtained in the receiver. The sp. gr. of the distillate may be at once taken without admixture with water. In this case, as there is only half of the original quantity, the distilled spirit will have twice the strength: hence the proportion of alcohol is determined by dividing the quantity per cent. by 2. Thus, four ounces of sherry yield two ounces of spirit, which, when mixed with two ounces of water, will have a sp. gr. of 0·9753=17 per cent. of alcohol. The distilled spirit, before the addition of its bulk of water, has a sp. gr. of 0·9511=34 per cent. of alcohol, and 34÷2=17 per. cent. of alcohol contained in the wine. These methods of determining the alcoholic strength of wines are applicable to ale, beer, and other weak alcoholic liquids.

Independently of the proportion of alcohol, the analysis of wine is directed to the amount of dry extract, the quantity of mineral matter, and the nature of the inorganic salts. The presence of tannic acid, grape-sugar, and other inorganic ingredients, may be determined by their appropriate tests. The following represents a recent analysis of a sample of dry sherry. The sp. gr. of the entire wine was 0·994. The alcohol, obtained by distillation from a measured quantity, when made up to its original bulk with distilled water, had a sp. gr. of 0·978 at 60°. According to the tables, this is equivalent to 15 per cent. by weight of absolute alcohol. The dry extract obtained by the evaporation of the wine amounted to 3·75 per cent. of its weight. This consisted chiefly of grape-sugar, coloring matter, acid tartrate of potassa, and tartrate of lime. The dry extract, when incinerated, left a white ash, which weighed 0·45 grains. The ash was slightly alkaline: it contained potassa, soda, lime, and a trace of alumina, with carbonic and sulphuric acids. In the entire wine, besides grape-sugar and coloring matter, tartaric, tannic, and sulphuric acids were found—the latter in comparatively large proportion, owing to the use of burning sulphur, for checking undue fermentation in the wine-manufacture. The constitution of this wine would therefore be, in 100 parts, as follows:—

Sp. gr. in the entire state	0·994
Alcohol	15·00
Dry saccharine extract	3·30
Mineral ash	0·45
Water, oil, ether and volatile products	81·25
	100·00

The comparison of weight with measure may be thus made. The sp. gr. represents in grains the weight of eighteen fluid drachms of the wine at 68°, namely, 994 grains, the same volume of water weighing nearly 1000 grains at this temperature.

The mixture of the distillate with the residue in the retort, however carefully the distillation may have been conducted, will not reproduce the wine with its original odor and flavor. This is owing to the loss or decomposition of the volatile oily matters and œnanthic ether during distillation.

The quality of wine, although for financial purposes estimated by its alcoholic strength, does not depend on the amount of alcohol, or of dry residue in one hundred parts, although the finest wines contain, generally speaking, a large proportion of solid matter. It depends chiefly upon the peculiar flavor imparted by the grape during fermentation, and the effects of age in improving and heightening this flavor. The amount of alcohol will depend on the quantity of fruit-sugar in the grape-juice, on the addition of starch-sugar, or glucose, to the must during fermentation, or of brandy after that process. The solid contents are generally small, except in sweet wines. Dr. Christison states, from his observation, that in Port and Sherry, when fit for drinking, the solid seldom exceeds three per cent., in Bordeaux wine they amount to about two and a half, and in Hock and Moselle to two per cent. only.

The results of analysis will be affected by the age of the wine, the degree to which fermentation has taken place, and other circumstances. The following table represents, chiefly as the result of recent analyses, the constitution of many wines which are now consumed in this country. The alcoholic strength is given by weight in absolute alcohol (sp. gr. ·794 at 60°). At this temperature and specific gravity, 49 parts of alcohol by weight are equivalent to 100 parts of proof spirit, by weight (sp. gr. ·920), or to 102·57 parts by measure. The alcoholic strength of vinous liquids is sometimes calculated in alcohol of a sp. gr. of ·825. At this sp. gr., however, alcohol is combined with 11 per cent. of water.

TABLE OF ANALYSIS OF WINES.

Name.	Spec. grav.	Alcohol in 100 by weight.	Dry extract in 100 by weight.	Ash in 100 by weight.
Port, 1820 (Muspratt)	0·9945	18·01	5·14	
Port, 1844	0·9977	17·00	6·20	0·30
Sherry	0·9060	17·30	5·70	0·70
Sherry (dry)	0·9940	15·00	3·75	0·45
Tarragona	1·0154	16·00	10·80	0·50
Gelopiga	1·0547	15·00	20·70	0·20
Bucellas	0·9934	16·00	3·30	0·40
St. Estephe	0·9930	10·00	2·00	0·30
"	0·9933	10·00	2·47	0·23
Haut Brion	0·9940	9·00	2·30	0·25
St. Emilion	0·9960	9·00	2·44	0·32
Beaujolais	6·9930	10·00	2·00	0·20
Sauterne	0·9955	7 50	1·32	0·10
Chablis	0·9912	9·00	1·60	0·10
Roussillon	1·0076	13·00	7·10	0·40
Steinberg (Geiger)	1·0025	10·87	9·94	
Rüdesheim	1·0025	12·65	5·39	
Tokay (Richter)	1·0201	12·10	10·60	
Malaga (Mayer)	1·0570	12·24	18·40	
Tent wine	1·1150	7·00	32·60	0·40
Champagne	1·0290	11·70	0·30	traces

In comparing the bulk of the wine with the weight, it may be observed that the sp. gr. represents the weight in grains and tenths of grains, of 18 fluid drachms, or 65 cubic centimetres. Thus, this quantity of port wine (1820) weighed 994·5 grains, the same volume of water weighing 1000 grains. In calculating the percentage of alcohol as proof spirit at 918, the amount in absolute alcohol should be doubled. Thus, 18·01 absolute alcohol in port wine (1820) are equivalent to 36·75 of proof spirit per cent.

SPIRITUOUS LIQUIDS.—Brandy, rum, gin, and whisky are spirituous liquids which contain about half their weight of alcohol, and are, therefore, nearly in the condition of proof-spirit.

They are obtained by distilling fermented liquors. They chiefly consist of alcohol and water, with a very small proportion of solid matter: they owe their peculiar odors and flavors to the presence of certain oily and ethereal products of fermentation. When genuine, they are neutral, and leave only a slight residue on evaporation. *Brandy* is the result of the distillation of wine; and its qualities vary with the kind of wine from which it is obtained, and the precautions with which it is distilled. It is frequently strongly colored with caramel.—*Rum* is distilled in the East and West Indies from a fermented mixture of molasses and water, with the skimmings of the sugar boilers, and the lees or spirit-wash of former distillations.—*Gin*, or *Geneva*, is prepared from different kinds of corn-spirit: it was originally largely imported from Holland, and was known as Hollands or Hollands' gin. Its flavor is derived from juniper-berries, or from the essential oil of juniper, which contributes to its diuretic quality. *Calamus aromaticus*, or sweet flag, and other flavoring articles, are occasionally used in its manufacture. The great gin-distillers sell it to the trade at about 20 per cent. over proof, but the retailers afterwards dilute and generally sweeten it. Various chemical substances are employed in its adulteration.—*Whisky* (a term said to be derived from the Irish *usquebaugh*) is also a corn-spirit, and, when genuine, derives its characteristic flavor from the malt used in its manufacture having been dried over peat or turf-fires; but this odor and flavor of burned turf, or peat-reek, is frequently given to raw corn-spirit by impregnating it with peat-smoke.—*Arrack*, or *Rack*, is a spirituous liquor prepared in various parts of India from the fermented juice of the cocoa-nut, and also from fermented infusion of rice. It has a peculiar flavor and odor, but in other respects, closely approaches in its characters to rum. It is said that a genuine arrack may be very well imitated by dissolving 10 grains of benzoic acid in a pint of rum.

There are many other alcoholic liquors, the preparation of which is peculiar to different places.—*Kirschwasser* is obtained in Switzerland, and in some parts of France, from bruised black cherries, fermented and distilled. —*Maraschino* is a similar liqueur, prepared also from a peculiar kind of cherry growing in Dalmatia.—*Noyau* and several analogous *liqueurs* are flavored with an essential oil containing more or less hydrocyanic acid, and often with that derived from bitter almonds, the kernels of peaches, apricots, &c., or from the leaves of laurels. Some of these compounds come under the denomination of *tinctures;* such, for instance, as *Curaçoa*, which is prepared by digesting orange-berries (the immature fruit) and bitter orange-peel with cloves and cinnamon in brandy: when this tincture is distilled, and afterwards sweetened, it constitutes *white Curaçoa.* These compounds are frequently called *Ratafias*, a term derived, like the word ratify, from *ratum* and *fio*, to make firm, or confirm. By *ratafia*, therefore, was originally meant a liquid drunk at the *ratification* of an agreement.

In the analysis of these spirituous liquids the distillation for the separation of alcohol must be carried on at a low temperature until nearly the whole of the liquid has passed over. The following table represents the results of recent analyses, the alcohol being estimated by weight and volume as absolute.

Name.	Sp. grav.	Alcohol in 100 by weight.	Dry extract in 100 by weight.	Ash in 100 by weight.
Whisky	0·9208	50·00	0·10	trace
Gin	0·9440	45·00	0·20	0·10
Brandy, Cognac	0·9300	46·00	1·40	0·20
“ common	0·9483	36·00	0·60	0·05
Rum	0·9260	48·00	0·90	0·10

CHAPTER XLVII.

ALCOHOL. ALDEHYDE. CHLOROFORM. METHYLIC, AMYLIC, AND OTHER ALCOHOLS.

Alcohol. Ethylic Alcohol ($C_4H_6O_2$).

The word *alcohol* signifies in Arabic a liquid or solid brought to its utmost perfection. By the careful distillation of any of the spirituous or fermented liquids described in the preceding chapter, the alcoholic portion may be separated from the less volatile matters, and the product is known in commerce as *Rectified Spirit of Wine.* Its sp. gr. is usually about 0·840 to 0·850, and it consists of alcohol combined with about from 17 to 20 per cent. of water: it generally contains traces of oily matters, and of some other impurities. The distillers commonly prepare a liquor called *wash*, for the express purpose of producing from it, rectified spirits. Instead of using pure malt, they employ chiefly raw grain, mixed with a small quantity only of malted grain. The water employed in the mash-tub is generally at a lower temperature than that adopted in brewing beer, and the mashing is longer continued. The wort is afterwards fermented with yeast, and then distilled for the production of proof-spirit and alcohol. In this state the product is called *malt-spirit.* Its specific gravity is from ·914 to ·936, and it contains about half its weight of alcohol. The oily products which are combined with the spirit and render it impure, are mostly less volatile than alcohol, so that when the process of rectification is carefully performed, they remain with the residuary water in the still or retort. Many precautions are requisite, both in conducting the distillation, and in the management and construction of the stills, so as to produce what is technically known as *clean spirit. Rectified spirit* thus obtained, varies in sp. gr. from ·835 to ·884, and contains from 85 to 65 per cent. of alcohol.

To obtain pure or *absolute* alcohol, rectified spirit is usually dehydrated, by distilling it with certain substances which have a strong affinity for water. Although the boiling points of alcohol and water greatly differ, it is impossible to separate the water from aqueous alcohol by distillation at a low temperature. The vapors of both pass over and are condensed together so soon as the liquid reaches a sp. gr. of 0·825. Among the substances used for dehydration, are carbonate of potassa, chloride of calcium, quicklime, and anhydrous sulphate of copper.

When common spirit of wine is employed, the first portions of water may be abstracted by adding to it dry carbonate of potassa until that salt ceases to be dissolved; the mixture is then frequently shaken, and when allowed to stand at rest, it soon separates into two portions, the uppermost being alcohol (of sp. gr. 0·825) and the lowermost an aqueous solution of the carbonate. The former is drawn off and poured upon a quantity of powdered quicklime, amounting to about half the weight of the alcohol, and previously introduced into a tubulated retort. This mixture may be left to digest for a day or two, and then slowly distilled in a water-bath, at a temperature of about 200°. Fresh burnt lime alone may be used without the previous employment of carbonate of potassa, the water being then absorbed and retained by the lime as hydrate. In place of lime an equal weight of fused chloride of calcium may be employed. Any color or odor possessed by the rectified spirit may be removed by the use of finely powdered animal charcoal.

Properties of Alcohol.—Alcohol is a limpid colorless liquid of an agreeable odor, and a strong pungent taste. It is quite neutral, and is not liable to undergo any change by keeping. The specific gravity of *absolute alcohol* is 0·794 at 60°. When spirit of wine is as far as possible dehydrated by simple distillation, its specific gravity is 0·825 at 60° (=89 per cent. of alcohol). The *rectified spirit* of the Pharmacopœia is directed to have a sp. gr. 0·838. The quantity of absolute alcohol contained in these and other commercial forms of alcohol and spirit of wine, will be seen by reference to the table given at p. 542. According to Despretz, the specific heat of alcohol is 0·52. Alcohol has never been frozen. Faraday exposed it to a temperature of 166° below 0°; it thickened considerably, but did not congeal (*Phil. Trans.*, 1845, p. 158). According to Mitchell, alcohol of 0·798 becomes oily at —130°, and at —146° flows like a melted wax; and alcohol of sp. gr. 0·820 entirely congeals in a bath of solid carbonic acid and ether (—166°). The boiling-point of alcohol of sp. gr. 0·7947 is 173° (Barom.

29·5). When of the sp. gr. 0·825 it boils at a temperature of 176° under the same pressure. In the vacuum of an air-pump, alcohol boils at common temperatures. The specific gravity of the *vapor* of alcohol (in reference to air = 1·000) was experimentally found by Gay-Lussac to be 1·6133: this nearly corresponds to its calculated specific gravity (*see* page 659). The latent heat of the vapor of alcohol is to that of the vapor of water as 332 to 531 (DESPRETZ).

Absolute alcohol has so strong an affinity for water as to absorb it from the atmosphere; it requires, therefore, to be kept in well-stopped bottles, as, after exposure, it undergoes a sensible increase of specific gravity; it is even apt to absorb a small quantity of water during its distillation. Alcohol does not appear to form any definite *hydrate:* for even the water, which passes over with it by distillation at a sp. gr. of 0·825, may be entirely separated by lime, carbonate of potassa, or any substance which combines with or dissolves in water. It may be mixed, in all proportions, with water, and while heat is evolved, a diminution of bulk (or increase of specific gravity) ensues. When alcohol and snow are mixed, there is, on the other hand, a diminution of temperature, as a result of the sudden liquefaction of the snow. The contraction in volume which ensues on mixing alcohol with water has been already described (p. 46): it is always attended with an increase of temperature. Thus equal measures of alcohol (sp. gr. 0·825) and water, each at 50°, afford, when suddenly mixed, a temperature of 70°; and equal measures of proof spirit and water, each at 50°, give, under similar circumstances, a mixture of the temperature of 60°. The greatest amount of heat and condensation is produced by the admixture of 1 equivalent (53·74 parts) of alcohol and 6 equivalents (49·84) of water. The mixture is reduced on cooling to 100 parts, and has a sp. gr. of 0·927.

Proof Spirit.—This is a weaker form of alcohol than rectified spirit. It is employed in reference to Excise regulations, and in pharmacy (*Spiritus tenuior*). In the latter, the sp. gr. is fixed at 0·920. It consists by weight at 60° of 49 parts of alcohol and 51 parts of water. The sp. gr. of Excise proof-spirit at 60° is 0·916. This corresponds nearly to equal parts by weight of alcohol and water. Such a mixture, according to Gilpin's tables, should have a sp. gr. of 0·917. The term *proof,* appears to be derived from the gunpowder-test. Spirit was poured over gunpowder and the vapor inflamed: if it fired the gunpowder it was over-proof; if it burnt without igniting the powder, owing to the residuary water rendering the powder damp, it was said to be under-proof. The weakest spirit capable of firing gunpowder was the proof-spirit of pharmacy, sp. gr. 0·920. Drinkwater gives the following table, showing the results of his experiments upon the composition of *proof-spirit.*

Alcohol and water.		Specific gravity at 60° F.	Bulk of mixture of 100 measures of alcohol + 81·82 water.
By weight.	By measure.		
Alcohol. Water.	Alcohol. Water.		
100 + 103·09	100 + 81·82	·91984	175·25
or in 100	or in 100		
49·24 + 50·76	54 + 46		

The *strength* of such spirituous liquids as consist of water and alcohol, is ascertained by their *specific gravity,* and for fiscal purposes it is determined by the *hydrometer;* but the only correct mode of ascertaining the specific gravity of liquids, is by weighing them in a delicate balance, against an equal volume of pure water of the same temperature. For this purpose a thousand-grain bottle may be employed. Small hydrometers are constructed to indicate, by flotation, proof-spirit, and a certain number of degrees above and below proof.

Alcohol is extremely inflammable, and burns with a pale bluish flame, scarcely visible in bright daylight; but the heat of its flame is very intense, as may be shown by suspending in it a coil of fine platinum wire, which soon becomes white-hot. It produces no smoky deposit upon cold substances held over it. The products of the combustion of alcohol are carbonic acid and water, the weight of the water considerably exceeding that of the alcohol consumed. According to Saussure, jun., 100 parts of alcohol afford, when burned, 136 parts of water, the production of which may be shown by holding a glass-jar over the flame until it is extinguished. Water is deposited on the sides of the jar, and carbonic acid is collected within it, a fact which may be proved by the addition of lime-water. The flame of alcohol may also be burned under a condensing-apparatus, the exit-tube at its extremity being turned down into a glass jar. It will then be found that a current of carbonic acid passes out of it: this may be rendered evident by lime-water, and the extinction of a taper. When alcohol is burned at a lower temperature than that required for its inflammation, as by the action of spongy or finely divided platinum, or by a hot platinum wire, as described at p. 54, the products of its combustion are different; the proportion of carbonic acid is less, and aldehydic and acetic compounds are formed.

The following table by Fownes represents the specific gravities of mixtures of alcohol and water. The proportion of absolute alcohol is given by *weight.*

Sp. gr. at 60°.	Percentage of alcohol.
.9991	0·5
·9981	1
·9965	2
·9947	3
·9930	4
·9914	5
·9898	6
·9884	7
·9869	8
·9855	9
·9841	10
·9828	11
·9815	12
·9802	13
·9789	14
·9778	15
·9766	16
·9753	17
·9741	18
·9728	19
·9716	20
·9704	21
·9691	22
·9678	23
·9665	24
·9652	25
·9638	26
·9623	27
·9609	28
·9593	29
·9578	30
·9560	31
·9544	32
·9528	33
·9511	34
·9490	35
·9470	36
·9452	37
·9434	38
·9416	39
·9396	40
·9376	41
·9356	42
·9335	43
·9314	44
·9292	45
·9270	46
·9249	47
·9228	48
·9206	49
·9184	50
·9160	51
·9135	52
·9113	53
·9090	54
·9069	55
·9047	56
·9025	57
·9001	58
·8979	59
·8956	60
·8932	61
·8908	62
·8886	63
·8863	64
·8840	65
·8816	66
·8793	67
·8769	68
·8745	69
·8721	70
·8696	71
·8672	72
·8649	73
·8625	74
·8603	75
·8581	76
·8557	77
·8533	78
·8508	79
·8483	80
·8459	81
·8434	82
·8408	83
·8382	84
·8357	85
·8331	86
·8305	87
·8279	88
·8254	89
·8228	90
·8199	91
·8172	92
·8145	93
·8118	94
·8089	95
·8061	96
·8031	97
·8001	98
·7969	99
·7938	100

Bleached bees-wax is sometimes employed as a test for the strength of spirits. It has a sp. gr. of ·960, and in spirit of this sp. gr., representing 29 per cent. of absolute alcohol, this substance indifferently floats or sinks. If the sp. gr. is lower, and the alcohol is therefore in greater proportion, it sinks: if, on the contrary, it is higher, and the water is in larger quantity, the wax floats. If a tube is half filled with water, and half with alcohol, the wax will sink through the latter, and float on the former, indicating its level. The slow diffusion of these liquids under such circumstances, will be proved by the wax maintaining its level for many weeks or months, provided the contents of the tube are not disturbed.

Graham has shown that alcohol may, in some instances, be combined with certain saline bodies, such as chloride of calcium, nitrate of magnesia, nitrate of lime, chloride of zinc, and chloride of manganese. The alcohol appears to be substituted for water of crystallization. Such combinations have been called *alcohates*. They are obtained by dissolving the substances by heat in absolute alcohol, and the compounds, more or less regularly crystallized, are deposited as the solution cools. They appear to be definite compounds, and in some of them, the alcohol is retained by an attraction so powerful, that it is not evolved at a temperature of 400° or 500°.

Alcohol dissolves nearly all the acids, mineral and organic, giving rise to an important and varied class of compounds. When a little sulphuric acid is mixed with alcohol, the mixture has no action upon any neutral carbonate, and yet it decomposes acetate of potassa, evolving acetic acid. A mixture of alcohol and hydrochloric acid does not act upon carbonate of potassa, but it decomposes the carbonates of soda, lime, strontia, and magnesia. A mixture of alcohol and nitric acid is without action upon carbonate of potassa, but it acts powerfully on the carbonates of lime and strontia, and slowly on the carbonates of soda, baryta, and magnesia. Alcoholic solutions of acetic and tartaric acid, decompose none of the carbonates: a similar solution of citric acid decomposes the carbonates of potassa and magnesia, but not the carbonate of baryta, strontia, or lime; while an alcoholic solution of oxalic acid decomposes carbonates of strontia, lime, and magnesia, but not carbonate of potassa. The addition of a small quantity of water does not affect these mixtures, for when a saturated solution of carbonate of potassa is mixed with an alcoholic solution of acetic acid, the carbonate is precipitated without effervescence (p. 50): an alcoholic solution, therefore, may appear neutral to certain tests, whilst, in reality, it is strongly acid.

Alcohol dissolves a small quantity of sulphur, especially at its boiling temperature, but the greater portion is deposited, on cooling, in small brilliant crystals. It also dissolves phosphorus, taking up about a 240th part at its boiling-point, and retaining a 320th part when cold. This solution is luminous in the dark on exposure to air, and produces a beautiful pale bluish flame, when poured upon hot water. Alcohol dissolves sulphide of carbon, and the solution is decomposed by the alkalies.

Alcohol is an important agent in organic analysis: it dissolves benzole, chloroform, ether, the resins, and a large number of the alkaloids, the vegetable acids, camphor, and all the essential oils. It dissolves some of the fatty acids, but not readily the fixed oils, excepting castor oil. It dissolves grape and fruit-sugar, but does not readily dissolve cane-sugar, and has no solvent action on starch and gum. It deoxidizes slowly a solution of permanganate of potassa, but rapidly when the mixture is heated, or some hydrochloric acid is added. It has no reducing action on the salts of silver or gold, or on precipitated oxide of copper when mixed with potassa. It readily reduces chromic acid to green oxide of chromium, when set free from a chromate by an acid (hydrochloric), and the mixture is heated. A solution of a chromate, rendered alkaline by potassa, is not reduced when heated with alcohol. As this alkaline solution is readily reduced by grape-sugar, the presence of grape-sugar in an alcoholic liquid may be determined by this, as well as by the copper-test (p. 528).

Potassium decomposes rectified spirit, if much water is present, with the ordinary phenomena of combustion. With strong spirit there is no combustion; and when sodium or potassium is placed on anhydrous alcohol, hydrogen is given off, and the metal disappears without combustion. A crystallizable compound is obtained from the liquid, which has been called sodium or potassium alcohol, or ethylate of soda or potassa. When potassium or sodium is heated with alcohol, carburetted hydrogen is evolved among the products.

Potassa and soda are soluble in alcohol, hence this liquid is sometimes resorted to for the purification of these alkalies. After a time, however, they begin to act upon each other, and complicated changes ensue; a carbonate of the alkali is formed, and carbonaceous matter is evolved on the application of heat; by their slow mutual action, acetic acid, a resin, and a species of brown extractive, appear to be formed. Ammonia and its carbonates are soluble at common temperatures in alcohol: it also absorbs in various proportions several other gases. Lithia, baryta, strontia, and lime, almost insoluble in alcohol, even in their hydrated states; so also are the fixed alkaline carbonates: but their sulphides are dissolved. The greater number of the chlorides, iodides, and bromides, which are soluble in water, are soluble also in alcohol, and with many of them, the definite alcoholized compounds above mentioned are produced (p. 543): but the sulphates are almost all insoluble; hence the use often made in the analysis of mixtures of salts, of the separative power of alcohol.

The uses of alcohol in the arts, and its applications to various economical purposes, are extremely numerous: to the chemist it is a most valuable species of fuel. Alcohol coagulates albumen and corrugates fibrin. It removes water from organic matter, and is employed as an antiseptic.

Composition.—When alcohol-vapor and oxygen are mixed in certain proportions, and the mixture is fired by an electric spark, a violent explosion ensues, and carbonic acid and water are the results: 2 volumes of alcohol-vapor, or 1 equivalent, require 6 volumes of oxygen, or 12 equivalents, for their perfect combustion; and 4 volumes of carbonic acid and 6 volumes of aqueous vapor result, ($C_4H_6O_2+12O=4CO_2+6HO$).

The analysis of absolute alcohol by oxide of copper gives results in accordance with these experiments. The following is the composition of this liquid:—

	Atoms.	Equiv.	Per cent.	Dumas.	Vol.
Carbon	4	24	52·65	52·17	4
Hydrogen	6	6	12·90	13·31	6
Oxygen	2	16	34·45	34·52	1
Anhydrous alcohol	1	46	100·00	100·00	2

For the calculated vapor-density of alcohol, see p. 517.

The equivalent 46, which is here assigned to alcohol, is generally adopted by chemical authorities. Some have proposed to double it, and others to quadruple it, upon hypothetical considerations; but no sufficient reasons have been advanced for these changes.

Tests.—The chief adulterating ingredient is water, the amount of which may be determined by distilling the liquid and taking the sp. gr. of the distillate. Alcohol is entirely volatile, and any residue will indicate the amount of impurity. The odor and taste of the liquid will enable a chemist to determine whether any essential oil, resin, or methylated spirit, is mixed with it. Absolute alcohol should not give a blue color to the white anhydrous sulphate of copper, and should yield no precipitate of silicic acid when a current of fluosilicic acid gas is passed into it (*see* p. 287). In cases of suspected *poisoning*, the liquid should be distilled by a water-bath, and the product rectified with fresh lime or carbonate of potassa. The alcohol, if present, may be drawn off by a few fibres of asbestos and burnt. If in sufficient quantity it will be detected by its odor, and by its solvent power on camphor. If in very small quantity, the heated vapor should be conducted through a tube containing a few fibres of asbestos moistened with a mixture of bichromate of potassa and strong sulphuric acid. If only a trace of alcohol is present, green oxide of chromium will be precipitated on the asbestos. Ether and pyroxylic spirit produce a similar decomposition; but these liquids are detected by their peculiar odors.

Other alcohols are enumerated: the Propylic (C_6H_7O,HO); the Butylic (C_8H_9O,HO); the Caproic ($C_{12}H_{14}O_2$), and the Caprylic ($C_{14}H_{18}O_2$). These are occasional products of the vinous fermentation, but are more abundantly produced in the fermentation of the marc or residue of the grape. Like amylic alcohol, these alcohols, which are colorless volatile liquids, do not readily combine with water, in which, among other properties, they differ remarkably from ordinary or ethylic alcohol. They form an homologous series of compounds: each contains two equivalents of oxygen; and the equivalents of hydrogen always exceed by two the equivalents of carbon.

ALDEHYDE ($C_4H_4O_2$).

This compound, which is also called *Acetic Aldehyde*, derives its name from the words *alcohol dehydrogenatus*, inasmuch as alcohol becomes aldehyde by the loss of 2 atoms of hydrogen. Aldehyde is one of the products of the decomposition of alcohol or ether, in passing the respective vapors through a red-hot tube, or in burning mixtures of ether or alcoholic-vapor and oxygen, at a comparatively low temperature without flame.

$$\underbrace{C_4H_6O_2}_{\text{Alcohol.}} + O_2 = \underbrace{C_4H_4O_2}_{\text{Aldehyde.}} + 2HO$$

It is best obtained in its pure state by the following process (LIEBIG, *Ann. Ch. et Ph.*, lix. 289): a mixture of 4 parts of alcohol (sp. gr. 0.844), 6 of oil of vitriol, 4 of water, and 6 of pulverized binoxide of manganese, is introduced into a capacious retort, and distilled through a condenser into a large receiver cooled by ice. When about 6 parts have passed over, or when the distillate has become acid, the process is stopped, and the product is put into a small retort with its own weight of chloride of calcium, and redistilled; this process is repeated, so as to yield about 3 parts of dehydrated aldehyde. The distillate, however, still contains acetal, ether, and alcohol; to free it from these, it is mixed with about twice its volume of ether, and saturated with dry gaseous ammonia, when a crystalline compound of aldehyde and ammonia gradually separates, which is insoluble in ether, and which may be dried in the air. Two parts of this compound are then dissolved in their weight of water, and the solution mixed with 3 parts of sulphuric acid previously diluted with 4 of water, and distilled. Considerable effervescence ensues during the evolution of the aldehyde, which requires to be passed through a good condensing apparatus; the distillate is finally dehydrated by the careful addition of a little chloride of calcium, and distilled at a temperature of about 87°.

Pure aldehyde is a volatile colorless liquid, of a peculiar ethereal, and at the same time suffocating odor: when its vapor is respired, it produces spasm of the glottis. Its sp. gr. is 0·79 at 65°: its boiling point is 68°, and the density of its vapor 1·53. It mixes in all proportions with water, alcohol, and ether, and may be separated from its aqueous solution by means of chloride of calcium. It is neutral to test-paper, but acquires acidity on exposure to air, in consequence of the absorption of oxygen and the formation of acetic acid, a change which is very rapid under the influence of platinum-black ($C_4H_4O_2+O_2=C_4H_3O_3,HO$). Heated with dilute nitric acid, it is also acetified, and nitrous acid is formed. With another atom of oxygen, it forms *aldehydic acid* ($C_4H_4O_3$). An aqueous solution of aldehyde heated with oxide, or a salt of silver, reduces the metal in the form of a brilliant film, and *aldehydate of silver* is found in solution ($2AgO+C_4H_4O_2=AgO,C_4H_4O_3+Ag$). This result and the odor are the best tests of its presence. Aldehyde is found in the distillation of wines dissolved in alcohol. When its vapor is passed over a heated mixture of hydrate of potassa and quicklime, acetate of potassa is formed, and hydrogen gas disengaged. The term aldehyde is now applied to analogous compounds obtained from the imperfect combustion of other alcohols. They are named after the acids which they produce by the absorption of 2 atoms of oxygen; hence the compound above described is sometimes called acetic aldehyde.

CHLORAL ($C_4Cl_3HO_2$) is a transparent, colorless, oily liquid, obtained by the reaction of dry chlorine on anhydrous alcohol and by subsequent distillation. Its sp. gr. is 1·5; its boiling-point 206°, and the density of its vapor is 5. It has an irritating odor, is soluble in water, and its solution is not affected by nitrate of silver. It is sometimes called *chloric ether*, a name which is also applied to hydrochloric ether, chloride of hydrocarbon (p. 254), and to a solution of chloroform in alcohol.

CHLOROFORM (C_2HCl_3).

Chloroform may be procured by distilling chloral with lime and water, or with solution of potassa. It is more readily obtained by distilling in a capacious retort, a mixture of 1 part of alcohol with 24 parts of water and 6 parts of dry chloride of lime. The temperature should not exceed 180°. The distillate consists of water and chloroform, and the process is arrested when about two parts have passed over. The chloroform is in the lowest stratum. It is separated from the water, shaken with sulphuric acid to purify it, and rectified by a second distillation.

Chloroform is a colorless, transparent, heavy, neutral liquid, having, when its vapor is diluted, a pleasant odor resembling that of apples. Its sp. gr., when pure, is 1·5: it boils at 140°, and the density of its vapor is 4·2. It is not inflammable. When its vapor is respired, more or less diluted with air, it soon induces insensibility, in the same way as, but more rapidly and effectually than ether-vapor; hence its use in the performance of painful operations, as originally suggested by Dr. Simpson, of Edinburgh. (*Pharm. Journ.* vii. 277 and 313.) When a few drops of chloroform are placed upon the hand, it speedily evaporates, and produces a great degree of cold. When poured upon water, the greater part of the liquid sinks in globules, which are of a milk-white appearance if the chloroform is not perfectly free from alcohol. In addition to chloroform, the products of this reaction are formate of lime, chloride of calcium, and water. Chloroform is so little soluble in water, that three drops added to nine ounces of distilled water, and well shaken, did not wholly disappear, although they imparted a strong odor to the liquid. With alcohol and ether it readily forms transparent solutions, which burn with a yellow smoky flame. Water added to the alcoholic solution causes a separation of the chloroform, which falls to the bottom of the vessel.

Chloroform readily combines with oil of turpentine, and with sulphide of carbon. It easily dissolves camphor, and the solution burns with a yellow smoky flame, having a green edge or border. It speedily softens and dissolves caoutchouc. It dissolves wax, cantharidine, amber, copal, and all the common resins. With red or black sealing-wax it makes a strong varnish. It has but a slight solvent action on sulphur and phosphorus. It dissolves iodine and bromine, forming deep red solutions. A few drops of chloroform shaken with an aqueous solution of iodine or bromine will remove either of these bodies, and the chloroform falls to the bottom of the vessel, acquiring a red color, the depth of which is proportioned to the quantity of either substance present. Chloroform is usefully employed either alone or in combination with ether, as a solvent for many alkaloids. 100 parts of chloroform dissolve of veratria, 58·49 parts: quina, 57·47: brucia, 56·70: atropia, 51·19: narcotina, 31·17: strychnia, 20·19: cinchonia, 4·31, and of morphia, 0·57.

Chloroform floats on concentrated sulphuric acid, which is only darkened by it at a boiling temperature, when the chloroform is rapidly dissipated in vapor. It slowly decomposes nitric acid in the cold, but at a high temperature deoxidation is rapid, and nitrous acid is abundantly evolved. It scarcely affects a solution of iodic acid, which acquires, after a time, only a faint pink color. It has no bleaching properties: it does not decompose iodide of potassium, nor does it dissolve gold, either by itself or when boiled with concentrated nitric acid. When nitrate of silver is added to it, there is no precipitate, the chloroform merely acquiring that milky opacity which it has when dropped into distilled water. If pure, it evaporates from the hand without leaving any disagreeable odor.

When the vapor of chloroform is passed over copper or iron, heated to redness, it is decomposed, a metallic chloride results, and carbon is deposited; but, according to Liebig, no inflammable gas is evolved. It is not decomposed by potassium; some bubbles of hydrogen are sometimes set free, but it may be distilled over the metal without change. When passed through a glass tube heated to full redness, its vapor is resolved into chlorine and hydrochloric acid, but no carbon is deposited. On this is founded a process for its detection.

Chloroform is represented by the formula C_2HCl_3, and is considered to be a terchloride of the compound radical formyle (C_2H). When the 3 atoms of chlorine are replaced by 3 of oxygen, formic acid is produced: hence the name chloroform. The liquid contains 89 per cent. of chlorine, but, unlike an ordinary chloride, it gives not the slightest indication of the presence of this element by the usual test.

METHYLIC ALCOHOL ($C_2H_4O_2$).

This compound has been long known under the name of *Wood-spirit*, or *Pyroxylic spirit*. It derives its present name from μέθυ, wine, and ὕλη, wood.

When wood is subjected to destructive distillation there is formed, besides tar, acetic acid, and other products, a variable portion, but not amounting on an average to more than about 1 per cent., of an inflammable and volatile liquid. This may be separated, to a certain extent, from the water and acetic acid, by distillation and separation of the first products; these, redistilled and rectified over quicklime, afford the *pyroxylic spirit*, or *methylic alcohol* of commerce. If it contain ammonia, it should be neutralized, by sulphuric acid, previous to its last rectification.

To obtain perfectly pure pyroxylic spirit, an excess of chloride of calcium is added, and the mixture is distilled in a water-bath so long as any volatile matter goes over. A compound of wood-spirit with chloride of calcium remains in the retort, to which a quantity of water, equal to that of the original spirit, is added, and the distillation then continued. The product which is now obtained, and which is pure pyroxylic spirit diluted by a little water, may be dehydrated by a final distillation off quicklime, or anhydrous sulphate of copper.

Pyroxylic spirit is the *alcohol* of the *methylic* series. It is a limpid liquid, of a penetrating odor, partaking of that of alcohol and acetic ether, with an aromatic taint which has been compared to peppermint. Its taste is hot and pungent. Its sp. gr. at 60° is 0·7398. It is very inflammable, and burns with a pale flame resembling that of alcohol. It boils at about 150°; if heated in a retort, even in a water-bath, the sudden escape of its vapor is troublesome: this may be prevented by the presence of a little mercury, which equalizes the distribution of heat. The density of its vapor is 1·125 (1·20 at 212°). When pure it is not altered by exposure to air or light, but when subjected to the slow action of platinum-black, it yields, together with other products, *formic* acid; not acetic acid, as is the case with alcohol. If pure it is quite neutral, and mixes in all proportions with water, alcohol, and ether, without becoming turbid; it does not form a black precipitate with protonitrate of mercury.

Chlorine acts less powerfully on pyroxylic spirit than on alcohol, and according to Dumas and Peligot, heat is required to accelerate their mutual action: it then gives rise to the production of two liquids of very different degrees of volatility; that which is least volatile forms a crystallizable compound with ammonia. According to Kane, the action of chlorine on this spirit, under the influence of light, is violent and even attended by inflammation; in the absence of light, the gas is quietly absorbed under the abundant production of hydrochloric acid, and a thick liquid is formed, composed of $C_6H_2O_2Cl_3$. Chloride of lime acts upon pyroxylic spirit as it does upon alcohol, and methylic chloroform is one of the products. Its solvent powers, in regard to *salts* closely resemble those of alcohol, and it has been stated that it may be substituted for alcohol in the preparation of fulminating silver, although the action is less violent, and the product smaller in quantity; but according to Dumas and Peligot, the product is really *oxalate*, and not fulminate of silver; so also it converts nitrate into oxalate of mercury. Sulphur and phosphorus are to a small extent soluble in it. It dissolves the resins, and may be used as an excellent substitute for alcohol in almost all varnishes; indeed, its superior volatility renders it preferable; but its offensive odor is objectionable. It is a powerful antiseptic, and has been found a most effectual preservative of animal matter.

Pyroxylic spirit has the formula of $C_2H_4O_2$, or as hydrated oxide of methyle of C_2H_3O,HO, or MeO,HO.

Methylated Spirit.—A mixture of 90 per cent. of alcohol and 10 per cent. of methylic alcohol, is much used in the arts and manufactures, as well as in medicine and chemistry, as a substitute for rectified spirit.

Methyle $Me(C_2H_3)$ is a gaseous body of a sp. gr. of 1·036. It is produced by decomposing iodide of methyl with zinc. It forms an oxide analogous to ether in composition.—*Methylic ether*, C_2H_3O. This oxide is a colorless gas of an ethereal odor, and has a sp. gr. of 1·59. It burns with a pale blue flame. In elementary composition it is isomeric with alcohol, for $2\,(C_2H_3O)$ are equal to $C_4H_6O_2$. Methylic ether is procured by distilling 1 part of wood-spirit with 4 parts of sulphuric acid. The gas may be collected over mercury, and the carbonic and sulphurous acids mixed with it, may be removed by potassa. Methyle forms a chloride, iodide, and bromide, as well as various other compounds, with the oxacids, analogous to those of ethyle.

AMYLIC ALCOHOL ($C_{10}H_{12}O_2$.)

Amylic Alcohol, or *Hydrated Oxide of Amyle* ($C_{10}H_{11}$,O+HO; or AylO) has long been known under the name of oil of potato-spirit; it is the *fusel-oil* of the Germans. It is now considered as the *alcohol* of the amylic series, the base of which is amyle ($C_{10}H_{11}$). It has hitherto been exclusively obtained as a product of fermentation, especially from potato-brandy. Balard (*Erdmann and Marchand's Journ.*, xxxiv. 123) found it, accompanying œnanthic ether, in the volatile oil obtained from brandy; it has also been detected in the spirit afforded by the fermentation of beet-root treacle. It is abundantly obtained from corn-spirit, in the process of its rectification upon the large scale (MEDLOCK, *Journ. Chem. Soc.*, i. 368).

When potato-brandy is distilled, and after the greater part of the alcohol has passed over, a milky liquid is obtained, which deposits the crude *potato-oil.* It is similarly obtained among the less volatile products of the distillation of corn-spirit of all kinds. This crude oil is purified by washing it with water, then drying it by means of chloride of calcium, and redistilling it; the portion which passes over at about 268° or 270°, is pure *amylic alcohol.*

It is a colorless liquid of a peculiar, nauseous, suffocating, and most persistent odor. It has an acrid taste; it burns with a blue flame, but is not very easily inflammable; its sp. gr. is 0·812 at 60°; it boils at 270°; the density of its vapor is 3·14. At 4° it forms a crystalline solid. It is sparingly soluble in water, but dissolves in all proportions in alcohol, ether, and in fixed and volatile oils. It dissolves iodine, sulphur, and phosphorus. When acted upon by oxidizing agents it yields *Valeric acid.* According to Cahours, it is resolved, under the influence of platinum-black, into Valeric acid and water. Its formula is $C_{10}H_{12}O_2$, or $C_{10}H_{11}O+HO$.

Amyle ($C_{10}H_{11}$,) Ay has been isolated by Frankland (*Journ. Chem. Soc.*, iii. 30). He obtained it by the action of zinc-amalgam upon iodide of amyle, under pressure. Amyle is a colorless pellucid liquid of an ethereal odor and burning taste; cooled down to 18° it becomes thick and oily, but does not solidify: its sp. gr. at 52° is 0·7704: the density of its vapor is 4·9062 (=5 vols. carbon vapor, 4·1461; +11 vols. hydrogen, 0·7601). It boils at 310°. It does not ignite at ordinary temperatures, but on being heated its vapor burns with a white smoky flame. It is insoluble in water, but mixes in all proportions with alcohol and ether. It is not affected by fuming sulphuric acid, but is slowly oxidized by fuming nitric acid, or by a mixture of nitric and sulphuric acids, when it acquires the odor of Valerianic acid. Amyle forms a hydride ($C_{10}H_{11}H$).

Like ethyle and methyle, amyle forms an oxide—*amylic ether* ($C_{10}H_{11}O$); and it combines with halogens, as well as with certain acids, to form compounds resembling the ethers of these radicals.

AMYLENE ($C_{10}H_{10}$).—When amylic alcohol is distilled with anhydrous phosphoric acid, this compound passes over as a colorless oily liquid. It is lighter than water; its boiling-point is about 102°. It is a hydrocarbon, isomeric with olefiant gas and etherine; but the density of its vapor is 5·06, which is 5 times that of olefiant gas; each volume of it therefore contains 10 volumes of hydrogen in combination with 10 atoms of carbon. It has been used, but unsuccessfully, as a substitute for chloroform in anæsthetic surgery: it has caused death in several instances.

CHAPTER XLVIII.

ETHER (C_4H_5O). OIL OF WINE. COMPOUND AND DOUBLE ETHERS.

THE term *Ether* is applied to a highly volatile liquid obtained by the action of sulphuric acid upon alcohol. This liquid is usually procured either by distilling a mixture of sulphuric acid and alcohol, or by allowing alcohol to drop gradually into the heated, and somewhat diluted acid.

Production.—Sulphuric acid, water, and alcohol, at a certain temperature, are necessary for the production of ether. Concentrated sulphuric acid mixed with diluted alcohol, or diluted sulphuric acid mixed with absolute alcohol, will equally produce ether, provided certain proportions are observed, and a certain temperature is maintained. The following process has been found to yield satisfactory results: A mixture of 8 parts by weight of concentrated sulphuric acid, and 5 parts of rectified spirit of wine of sp. gr. 0·834, is introduced into a large flask, connected with a proper condensing apparatus and receiver, and the mixture is heated by means of a lamp until it attains a temperature of 300°. The rectified spirit is then allowed to drop into the heated mixture through a long funnel, and by adjusting its quantity on the one hand, and regulating the degree of heat on the other, the temperature of 300° is maintained as steadily as possible, taking care at the same time that the liquid in the flask is kept in rapid ebullition. Under these circumstances the bulk of this liquid may be maintained unchanged for several hours, and every drop of alcohol which falls into it is instantly converted into ether and water, the mixed vapors of which pass through a tube into a condenser. The receiver is ultimately filled with water and ether, the latter floating upon the former.

The principal point to be attended to in this process, is the maintenance of a steady temperature at or about 300°, and of rapid or even violent ebullition. The limits of the ether-producing temperature are between 260° and 310°, and the success of the operation is well insured by the use of oil of vitriol and spirit of wine, in the above proportions and of the described strength. If more alcohol, or a weaker acid be used, so as to occasion the boiling-point to fall below 260°, little else than unchanged alcohol distils over; and if, by the employment of too much oil of vitriol, the boiling-point rises up to or above 320°, in place of ether, oil of wine and olefiant gas are generated, together with variable quantities of other products.

The proportions recommended by Mitscherlich are, 100 parts of concentrated sulphuric acid (which already contains 18·5 of water) diluted with 20 parts of water, and mixed with anhydrous alcohol, in the proportion of 50 parts to every 100 of concentrated acid. To this mixture heat is applied, and it is kept boiling until the thermometer within the flask indicates 284°: two strips of paper are then pasted upon opposite sides of the flask containing the mixture, to indicate exactly the bulk of its contents, by showing the level of the liquid within it; alcohol is then allowed to flow in by a funnel-tube, the supply being so regulated as to maintain the boiling-point at 284°. The temperature for etherification, according to Mitscherlich, is between 284° and 302°. The distillate obtained by this process, separates into two parts, the lighter stratum being ether with a little alcohol and water; and the heavier, water with a little alcohol and ether. If the process has been carefully conducted, the weights of the water and ether exactly correspond to that of the alcohol consumed. In an experiment on a large scale, the proportions obtained in the distillate were 65 ether, 18 alcohol, and 17 water. Careful manufacturers obtain from 100 parts of rectified spirit, containing 76 parts, by weight, of absolute alcohol, 60 parts of ether, of the sp. gr. 0·727: according to calculation, they should obtain 58 parts of ether of 0·724.

The ether of commerce almost always contains alcohol, which materially affects its density; sometimes it also contains water, which is the case with what is termed *washed ether;* and if ether has been long prepared, it is often slightly acid, and leaves a peculiar odor when rubbed upon the hand. In order to procure from the distillate perfectly *pure ether,* it must be well shaken in a close vessel with about twice its bulk of water, and allowed to separate upon the surface of the mixture; it is then poured off, and a sufficient quantity of well-burned lime added to it, by which the water which it had acquired by the agitation, is abstracted. The mixture of ether and lime is then distilled by a water-bath, care being taken to prevent all escape of vapor, and to keep the condensing-receivers cold: the first third that distils over may be considered as *pure ether*, free from alcohol and water. Commercial ether may be purified by agitating it with milk of lime, and then distilling it from a water-bath by a gentle heat; the first distillate is then shaken with water to separate alcohol, and the resulting aqueous ether subsequently dehydrated by distilling it off quicklime, or chloride of calcium.

The *chemical changes* which take place in the production of ether have been variously described. The alcohol is entirely resolved into ether and water ($C_4H_6O_2 = C_4H_5O + HO$), but sulphuric acid does not operate by simply abstracting the elements of water, since ether is equally produced at the proper temperature (284° to 302°) by the reaction of diluted sulphuric acid on absolute alcohol. One theory assumes that by the admixture of sulphuric acid and alcohol in certain proportions, *Sulphovinic acid* is produced; and that at a certain temperature, this acid is simply resolved into ether and a mixture of sulphuric acid and water. Sulphovinic acid has been regarded by Liebig as a bisulphate of alcohol ($C_4H_6O_2 2SO_3$), and by Regnault as a bisulphate of ether with 2 atoms of water ($C_4H_5O,2SO_3 + 2HO$). Whichever view is adopted, it is obvious that this compound contains all the elements necessary to the production of ether, when the mixture is exposed to the temperature required for its decomposition. The researches of Graham have, however, proved that the production of sulphovinic acid is not necessary to the formation of ether. When a mixture of oil of vitriol and alcohol is exposed in a sealed tube to a temperature ranging from 284° to 302°, no charring occurs, but the liquid divides itself into a light stratum which is nearly pure ether, and a heavy stratum consisting of alcohol, water, and sulphuric acid (*Journ. Chem. Soc.*, iii. p. 24). These results confirm the original view of Mitscherlich, that alcohol is, under certain fixed conditions, simply resolved into ether and water by a catalytic, or polymerizing, action of sulphuric acid (*see* p. 55). The acid which remains in the retort is unchanged in properties, and unaltered in quantity. A certain proportion of acid is necessary in the process, in order to maintain the liquid in the retort or flask at the requisite temperature. Sulphuric acid exerts a similar catalytic action on oil of turpentine: it splits this oil into two other hydrocarbons—terebene and colophene—one of which has a higher boiling point and a greater vapor-density than oil of turpentine. This product, as in the case of ether, does not form any combination with the acid.

As an additional proof that ether is produced independently of the conversion of alcohol into sulphovinic acid, it may be stated that the proportions of alcohol and sulphuric acid, which yield the greatest amount of sulphovinic acid, do not yield the largest proportion of ether. One part of sulphuric acid to 6 or 8 parts of alcohol, yields the largest quantity of ether and but little sulphovinic acid: the proportion of sulphuric acid must be greatly increased, in order to produce sulphovinic acid.

Other acids act in a similar manner. Thus, when alcohol is heated to a high temperature with a concentrated solution of phosphoric acid, it is split into water and ether. In this case the water is retained by the acid, and when this is sufficiently hydrated, its decomposing action on alcohol ceases. Certain chlorides and fluorides also produce this conversion. The anhydrous chloride of zinc dissolves to a great extent in alcohol. When this solution is distilled, alcohol first passes over, and as the temperature rises, ether and water are obtained as products in the receiver.

Properties.—Ether is a highly volatile, transparent, colorless, limpid liquid, of a peculiar penetrating odor, and a pungent and sweetish taste. It is highly exhilarating, and produces a remarkable species of intoxication when its vapor is respired mixed with air; by the proper management of the inhalation, a continuous insensibility to pain may be maintained. This application of ethereal vapor was at one time resorted to in the performance of surgical operations; but as an anæsthetic, the vapor of chloroform is now preferred. Ether is neither acid nor alkaline; it has a highly refractive power in regard to light, and is a non-conductor of electricity. It should not redden litmus when pure. The evaporation of this liquid produces intense cold. When a few drops of ether covering a drop of water are blown upon by a blowpipe the water freezes, in consequence of the rapid evaporation of the ether. The vapor has been employed for the artificial production of ice on a large scale, the evaporation of the liquid being accelerated by means of an air-pump. *In vacuo* this liquid boils at the lowest temperature. A mixture of it with solid carbonic acid causes the thermometer to sink to —166° (pp. 74, 252). The sp. gr. of ether varies greatly with the temperature. We found, at a temperature of 60°, that absolute ether, washed and distilled over quicklime, had a sp. gr. of 0·713. It is more commonly met with of a sp. gr. of 0·720. This liquid is so affected in its volume by temperature that 1000 parts at 96° are reduced to 968·2 at 60°, and to 948· at 33°.

At mean pressure, ether boils, according to Gay-Lussac, at 96·5. Ether of the sp. gr. of ·720 may be said to boil, under a pressure of 30 inches, at 98°. Upon this subject, however, authorities vary a little, in consequence of variations in the density of the ether, and also of barometrical pressure, circumstances which easily influence the boiling-point of this liquid. The extreme volatility of ether renders it impossible to pour it from one vessel to another without losing a portion by evaporation, and its vapor, in consequence of its density, may be seen to fall from the liquid: it is this which renders it so dangerous to expose ether near to, and especially above, the flame of a candle. The sp. gr. of the vapor, at mean pressure and temperature, is 2·5860 in reference to air as=1. At the temperature of 212°, 1 volume of ether gives 212 volumes of vapor. The density of the vapor may be well shown by dipping a flock of cotton into ether, and placing it within a glass tube of about an inch diameter, and 18 or 20 inches long; the vapor will descend and escape from the lower end of the tube, where it may be inflamed by a lighted taper, but none rises to the upper end of the tube. If the lower end of the tube be drawn into a point and bent upwards, the ether vapor may there be burned in the manner of a gas-light. The vapor of ether, poured from a wide-mouthed bottle through a long funnel, will readily fall, and, when ignited, burn at the end of the funnel. If two or three drachms of ether are placed in a quilled receiver on a stand, and the vessel is slightly inclined, the ether vapor will fall out of the long narrow tube, and may be burnt like a jet of gas. Its density is shown by depressing the tube, when the flame will be much increased. If raised, the flame is diminished, and ultimately extinguished. This proves the gravitating power of the vapor. Its great inflammability may be shown by boiling two or three drachms of ether violently in a Florence flask, and igniting the vapor as it issues. It burns in a large column of flame, with a light like that of coal-gas. Ether may be poured upon a large surface of water, and its vapor burnt on this liquid in a sheet of flame.

The elastic force of the vapor may be shown by letting a drop or two of ether pass into the vacuum of a barometer, when it instantly depresses the mercury several inches, more or less according to the temperature: hence also, when thrown up into gases standing over mercury, it greatly augments their bulk.

Pure anhydrous ether does not freeze. Faraday failed in congealing this liquid, although he exposed it to a temperature of 166° below 0°. (*Phil. Trans.* 1845, p. 158.)

When ether is inflamed it burns with a bright and slightly sooty flame, leaving no residue, and producing carbonic acid and water ($C_4H_5O+12O.=4CO_2+5HO$). These products may be collected by holding the mouth of a clean jar over a flame of burning ether. Water is condensed on the sides of the jar, and carbonic acid is collected in the interior. When lime-water is poured into the jar the presence of carbonic acid is proved by the liquid becoming milky white. Aldehyde and water, as well as acetic acid, are among the products of combustion at a low temperature ($C_4H_5O+2O=C_4H_4O_2+HO$). By passing ether into a jar supplied with a jet and stopcock, standing over warm water, its vapor may be burned at the jet. If its vapor is mixed with about 10 volumes of oxygen it explodes violently by an electric spark; but with smaller quantities of oxygen, or with air, this combustion is only imperfect. If a little ether is poured into a bladder full of air, supplied with a stopcock and jet, the mixture of air and ether vapor may be burned at the jet with a brilliant flame, without risk of explosion.

Exposed to air and light, as in bottles which are frequently opened, ether absorbs oxygen as ozone: it acquires bleaching properties, and is less capable of dissolving fixed oils. As one of the results of this absorption of oxygen, acetic acid is produced. The presence of this acid is not at first apparent, because it forms acetic ether, but it gives to the ether a peculiar odor, and in time it becomes acid to tests. The best method of preserving ether is to keep it in small well-stopped bottles, quite full, and in a dark place. In contact with alkaline bases, this conversion of ether into acetic acid takes place more rapidly.

When ether vapor is passed over red-hot platinum wire, or when red-hot platinum wire is plunged into a bottle of air containing a little ether vapor diffused in it, the metal continues to glow, and acetic and aldehydic acids are produced. When a stout rod of platinum, copper, iron, or glass, is heated to dull redness, and introduced into the mixture, ozone is produced at the expense of a part of the oxygen, and the ether is altered in properties. It will now slowly bleach a weak solution of sulphate of indigo (p. 102).

Ether is soluble in alcohol and chloroform in all proportions, but has only a limited solubility in water. Nine parts of water dissolve one part of ether. On this difference is based the separation of alcohol from ether, as well as the detection of that liquid in commercial samples. When a mixture of alcohol and ether is shaken with water the mixture separates into two layers, each of which contains the three liquids. The upper layer contains a large excess of ether, the lower a large excess of water, with the greater part of the alcohol with which the ether was mixed. By repeated washing, the whole of the alcohol may be removed. Ether which has thus been washed retains about a tenth part of water; or, according to Liebig, 36 parts of pure ether dissolve one part of water. From this it may be freed by distillation with quicklime, anhydrous sulphate of copper or dry chloride of calcium. A mixture of alcohol, ether, and ethereal oil is known under the name of *Hoffmann's anodyne liquor*, or spirit of ether. Such a mixture is employed in photography as a solvent for pyroxyline.

Ether dissolves a small quantity of sulphur (1-80th), which is not thrown down by the addition of a little water; the solution smells of sulphuretted hydrogen, and by slow evaporation deposits regular crystals of sulphur. Ether dissolves more than 2 per cent. of phosphorus (1-37th); the solution when concentrated by evaporation, deposits crystals of phosphorus: it is luminous in the dark when in contact of air, and if poured upon hot water produces a brilliant column of luminous vapor. Exposed to air, this solution becomes acid, and phosphorus is precipitated when it is mixed with water or alcohol; it gradually deposits red phosphorus when exposed to light. Ether does not dissolve potassa or soda, or their carbonates.

The fixed and volatile oils, many of the resins, caoutchouc, various forms of extractive, the alkaloids, and some other vegetable principles, are more or less soluble in ether; hence ether is often employed in the analysis of organic products, as a means of separating their proximate principles from each other. When mixed with chloroform, its solvent power on certain alkaloids is much increased. Such a mixture is employed as a solvent for strychnia. Many metallic salts are soluble in ether, and especially the chlorides of gold, platinum, iron, and uranium; the property which ether has of abstracting these salts from their aqueous solutions, has been adverted to under the history of the respective metals. Potassium and sodium are converted into potassa and soda by contact with ether, and hydrogen is disengaged.

A small quantity of sulphuric acid added to ether produces no effect, but a mixture of equal parts of ether and the acid blackens, and yields, on distillation, oil of wine, olefiant gas, acetic and sulphurous acids, and water; it leaves a resinous matter and charcoal. Anhydrous sulphuric acid decomposes ether, and produces, according to Liebig, "isethionic and althionic acids, oil of wine, and sulphate and bisulphate of oxide of ethyle; if heat be used, these products are decomposed, and sulphate of oxide of ethyle, oil of wine, water, and ether, together with acetic, formic, and sulphurous acids, carbonic oxide, and olefiant gas, pass over."

Heated with nitric acid, ether yields, according to Liebig, carbonic, acetic, formic, and oxalic acids, as well as aldehyde.

When a little ether is introduced into chlorine, the gas is absorbed, and peculiar compounds result. When bubbles of chlorine are passed into ether, they often cause inflammation, and when a small quantity of ether is poured into a jar of gaseous chlorine, and a lighted taper is applied, hydrochloric acid is formed, and carbon is set free, sometimes with explosion.

Iodine and bromine are soluble in ether, and gradually react upon and decompose it. The solution of iodine in ether is dark brown, and soon gives rise to the production of hydriodic acid. When ether is saturated with bromine, and the mixture is left for ten or twelve days, it is entirely decomposed; the products are, 1, formic acid(?); 2, hydrobromic acid; 3, hydrobromic ether; 4, heavy bromic ether; 5, bromal. The first four products may be separated by distillation, and the *bromal* remains ($C_4HO_2Br_3$): it may be purified by mixture with water, and in the course of twenty-four hours crystals of hydrate of bromal are formed. When this hydrate is boiled with an alkaline solution, 2 atoms are resolved into 2 atoms of formic acid, 2 of bromoform, and 6 of water.

Composition.—The vapor of ether, when passed through a red-hot tube, is decomposed: carbon is deposited, and water and aldehyde are among the products. When the vapor is analyzed by passing it through red-hot oxide of copper, the results furnish the following elementary composition:—

	Atoms.	Weights.	Per cent.	Vols.	Sp. gr.
Carbon	4	24	64·87	4	1·6584
Hydrogen	5	5	13·51	5	0·3455
Oxygen	1	8	21·62	½	0·5528
Ether	1	37	100·00	1	2·5567

The specific gravity of ether vapor compared with air is 2·5573, and its calculated density is in accordance with this result. Compared with hydrogen, the sp. gr. of ether vapor is 37; its volume equivalent is 1. If oxygen is assumed to be 16, the equivalent of ether must be doubled. Its relations to alcohol and other bodies would thus be disturbed, and the formulæ for the various ethers would be rendered unnecessarily complex.

Tests.—Ether may be identified by its odor and inflammability, as well as by the color of its flame and the products of combustion.

Ether is commonly regarded as an oxide of the compound radical *Ethyle* (C_4H_5). With an atom of water it forms alcohol, which is therefore a hydrated oxide of ethyle. Ethyle combines with the halogens and ether, as its oxide, combines with the oxacids. Dr. Frankland isolated this radical by the action of zinc on iodide of ethyle. (*Journ. of Chem. Soc.*, ii. p. 263.) He describes it as a colorless gas, of a slightly ethereal odor, burning with a brilliant white flame, and of a sp. gr. $=2·00394$. It is not liquefied at 0°, under atmospheric pressure, but under a pressure $=2·25$ atmospheres, at 37°, it becomes a colorless, transparent, mobile liquid; it is absorbed by alcohol, which evolves it again on dilution. In Frankland's experiments, the theoretical result of the decomposition of the iodide of ethyle, namely, $C_4H_5I+Zn=ZnI+C_4H_5$, was never attained, but a portion of the ethyle was always resolved into elayle and methyle, $C_4H_5=C_2H_2+C_2H_3$; so that the action of the zinc upon the iodide of ethyle, at the temperature required for its decomposition, namely 302°, may be represented as follows:—

$$2[C_4H_5I]+2Zn,=2ZnI,+C_4H_5+C_2H_2+C_2H_3.$$

The anhydrous, does not readily pass to the state of hydrated oxide of ethyle. Thus, ether may be shaken with water, and kept long in contact with this liquid without producing alcohol. The dehydration of the oxide (alcohol) is also effected in a remarkable manner by sulphuric acid, and this acid does not combine with the oxide as it is produced. The anhydrous oxide and water are distilled over together.

HEAVY OIL OF WINE. *Sulphatic Ether. Oleum Æthereum.*—When the distillation of a mixture of sulphuric acid and alcohol is carried beyond the point at which ether ceases to come over, a liquid, looking like oil, is obtained, to which the above names have been applied; when washed, it has a bitter aromatic flavor. It has long been known under the name of *oil of wine*, and was formerly regarded as analogous in composition to the volatile oils.

It may be prepared by distilling a mixture of 1 part of alcohol, and 2·5 parts of concentrated sulphuric acid. The oil in the distillate is separated from the water, and is purified by placing it *in vacuo* with two vessels, the one containing hydrate of potassa, and the other strong sulphuric acid. Its formula is C_4H_5O,SO_3. It is therefore, in constitution, a sulphate of the oxide of ethyle, or sulphuric ether.

The oil is of a yellow color, has a penetrating aromatic odor, and a sp. gr. of 1·133; it is soluble in alcohol and ether, but not in water. It cannot be distilled without decomposition; at 270° it is converted into alcohol, sulphurous acid, and olefiant gas. When long boiled with water, it is converted into sulphovinic acid and alcohol, and an oily hydrocarbon which floats on water. This is *light oil of wine*, or *etherole;* it resembles olive oil, and has a sp. gr. of 0·920.

Numerous ethers are produced by the action of a variety of acids upon alcohol. These are called *compound ethers.*

HYPONITROUS ETHER.—*Nitrous Ether* (C_4H_5O,NO_3).—This is procured by mixing and carefully distilling at a gentle heat, equal weights of alcohol (0·820) and of nitric acid (1·30). One hundred parts of this mixture yield 10 parts of rectified ether. It is a highly volatile inflammable liquid, sp. gr. 0·947 at 60°: it boils at 70°, and its vapor has a sp. gr. of 2·627. It is neutral, but by exposure to light in contact with water, it becomes acid.

NITRIC ETHER (C_4H_5O,NO_5).—A mixture of nitric acid and alcohol, when heated, or even allowed to stand, invariably produces hyponitrous ether, with a violent action. In order to prevent the formation of hyponitrous acid, about one per cent. of nitrate of urea is added to equal weights of nitric acid (1·4) and alcohol (0·842). The mixture is gently heated, and seven-eighths are distilled over. The nitrate of urea is unchanged, and may be repeatedly used. The rectified product has an agreeable odor, distinct from that of hyponitrous ether. It has a sweet and slightly bitter taste: its sp. gr. is 1·112, and it boils at 185°. It is insoluble in water, but soluble in alcohol, from which it is again precipitated by water.

ACETIC ETHER ($C_4H_5O,\bar{A}c$).—When an acid does not directly resolve alcohol into water and ether, the conversion may be effected, and a new ether produced by distilling one of the salts of the acid with alcohol and sulphuric acid. Thus three parts of acetate of potassa, three of absolute alcohol, and two of sulphuric acid, distilled to dryness, yield a product which, when rectified by redistillation with sulphuric acid and by the action of lime and chloride of calcium, is called acetic ether. This liquid boils at about 165°. Its sp. gr. is 0·89, and the density of its vapor is 3·03. It has a peculiarly agreeable odor, and appears to exist in and contribute to the odor and flavor of certain wines. It burns with a yellowish flame, and acetic acid is developed by its combustion. Water dissolves about one-seventh of its weight of this ether, and the solution is decomposed by potassa, giving rise to an acetate and to alcohol. Ammonia has no action upon it. It is soluble in all proportions in alcohol and in ether.

HYDROCHLORIC ETHER (C_4H_5Cl).—*Muriatic Ether. Chloride of Ethyle.* —This may be obtained by subjecting to careful distillation a concentrated solution of hydrochloric acid gas in alcohol; or a mixture of 1 part of alcohol, 1 of sulphuric acid, and 2 of fused and finely-powdered chloride of sodium. In all these cases the ether passes over: it should first be transmitted into warm water, by which its adhering acid and alcohol are abstracted, and its vapor may then be condensed by conducting it through a cold tube, and receiving it in a bottle surrounded by ice and salt. Hydrochloric ether is a limpid, neutral, colorless liquid, of a peculiar penetrating odor, and a sweetish acrid taste. Its specific gravity is 0·874 at 42°; it boils at about 60°; and the specific gravity of its vapor is 2·219. When cooled down to —10°, it crystallizes in cubes. It is soluble in about 50 parts of water, and in all proportions, in alcohol and ether. It dissolves sulphur and phosphorus, as well as the fixed and volatile oils.

IODINE and BROMINE produce with alcohol, ethers analogous to the hydrochloric. They have the formula C_4H_5I and C_4H_5Br.

Hydriodic Ether, or *Iodide of Ethyle*, is obtained by the distillation of a mixture of alcohol, iodine, and phosphorus. It is a colorless liquid of a penetrating ethereal odor, of a sp. gr. of 1·94 at 61°. It boils at 148°; the sp. gr. of its vapor is 5·4. It is not inflammable, but when dropped on red-hot charcoal it gives off a purple vapor. It is decomposed at a red heat. It is dissolved by alcohol, but not readily by water. This liquid possesses an interest as being the source of the compound radical ethyle (page 555). *Hydrobromic Ether* is prepared by a similar process. Fluorine, cyanogen, sulphocyanogen, and even sulphur, form compounds with ethyle of the nature of ethers. These are obtained by various complex processes. *Hydrosulphuric Ether* or *Mercaptan* (C_4H_5S+HS), is procured by distilling a concentrated solution of hydrosulphate of sulphide of barium with sulphovinate of baryta. It is a colorless liquid, of a strong odor, resembling that of garlic. It is not very soluble in water, but is dissolved by ether and alcohol in all proportions. Its sp. gr. is 0·832: it boils at 97°, and the density of its vapor is 2·14. It has a powerful affinity for mercury: it decomposes corrosive sublimate, forming mercaptide of mercury: hence the name mercaptan (*mercurium captans*).

Other ethers are formed by the combination of oxide of ethyle with many anhydrous acids—*e. g.*, the perchloric, silicic, boracic, oxalic, carbonic, arsenic, cyanic, hydrocyanic, formic, benzoic, succinic, and citric acids. These are for the most part procured by distilling a mixture of alcohol and hydrochloric or sulphuric acid with the respective acids or their salts.

Double ethers are those in which the elements of ordinary ether are combined with the ethers of the amylic or methylic series.

Compound ethers are found ready formed in plants and fruits, and to the presence of these, their odors and flavors are frequently due. They may be artificially imitated. When dissolved in a large quantity of alcohol, these ethers lose their offensive odor, and form various essences for giving perfume and flavor. Thus *pine-apple oil* is butyric ether, $C_4H_5O,C_8H_7O_3$. It may be produced from butter, or by the reaction of alcohol on impure glycerine. *Essence of melons* is ether combined with one of the acids of cocoa-nut oil, and *essence of quinces* is *pelargonic ether*, $C_4H_9O,C_{18}H_{17}O_3$. This is considered to be identical with œnanthic ether, which gives the bouquet to wine (page 535). *Pear-oil* is an alcoholic solution of the acetate of amyl, $C_{10}H_{11}O,C_4H_3O_3$, and *apple-oil* is the valeriate of the same radical, $C_{10}H_{11}O,C_{10}H_9O_3$. The *oil of winter-green* is the salicylate of methyl, $C_2H_3O,C_{14}H_5O_5$.

CHAPTER XLIX.

CELLULOSE. PYROXYLINE. WOOD. COAL. BITUMEN. PRODUCTS OF THE DECOMPOSITION OF WOOD AND COAL.

WOODY FIBRE. CELLULOSE. LIGNINE.

THE term *cellular matter*, or *cellulose*, has been applied to the pure base of woody fibre. The varieties of woody matter differ in color, texture, and induration; but when freed from various foreign matters, they leave a white translucent residue, insoluble in water, alcohol, and ether, and convertible, by sulphuric acid, into a substance having some of the characters of starch, and then into gum and sugar. Certain piths, linen, cotton, filtering paper, and some other allied substances, are nearly pure cellulose. Weak acids and alkaline liquids, and a weak solution of chlorine, have scarcely any action on it, but they change, combine with, or decompose it when concentrated, and some of these reactions are very important: when, for instance, clean linen or cotton rags are acted on by cold sulphuric acid, a magma is formed, which if immediately saturated by carbonate of baryta, or lead, yields insoluble sulphates, together with soluble *sulpholignates.* These salts appear identical with those of the sulphoglucic or sulphosaccharic acid, derived from the action of sulphuric acid on glucose. This magma is also blued by iodine. If it be much diluted and boiled, it yields dextrine, and ultimately glucose. By this action of sulphuric acid upon paper, a useful material now known as *vegetable parchment*, is obtained. It is prepared by steeping thick unsized paper in a mixture of equal parts of sulphuric acid and water, at a temperature of 60°, then washing it well in cold water and drying it. It is translucent, tough, and nearly impermeable to water, forming a useful substitute for common parchment or vellum. The following is another method of preparing this parchment: Two parts, by measure, of the strongest sulphuric acid are mixed with one part of water. These proportions are material: if the acid is weaker, the fibre of the paper is converted into gum, if stronger it is corroded. White blotting-paper is thoroughly soaked in the mixed acid and water, and immediately removed. It is then transferred to a large quantity of water containing a little ammonia, and after thorough washing it is dried. In this conversion the fibre undergoes no chemical change. The molecular condition of the paper is simply altered by the pores being filled up. The influence of a slight increase in the water may be thus shown. If the unsized paper is wetted in spots before it is immersed in the acid mixture, the wetted parts are destroyed while the remainder of the paper is parchmented. The substance is now put to some important uses in the arts.

PYROXYLINE. *Gun-cotton.*—This remarkable substance, discovered in 1846 by Schoenbein, is prepared by dipping clean carded cotton, well dried, into a mixture of 3 volumes of nitric acid (sp. gr. 1·5) with 5 of sulphuric acid. The concentrated commercial acids answer the purpose: the mixture is allowed to cool, and small portions of cotton should be used at a time, and completely immersed, so as to avoid elevation of temperature: in 10 or 20 minutes the cotton may be withdrawn (the excess of acid pressed out), and thoroughly washed in water containing a little ammonia; it is then cautiously dried, at a temperature not exceeding 200°. 100 parts of cotton thus treated yield about 170 of dry gun-cotton. Clean paper, the purer varieties of sawdust, and other forms of ligneous matter, produce similar compounds. Pyroxylic paper is remarkable for the intensity of its electricity when slightly rubbed. Well prepared pyroxyline resembles the original cotton in appearance, but is more harsh and brittle to the touch, and highly electric; its extreme combustibility is very remarkable; inflamed in the open air it flashes off without smoke, smell, or residue; it takes fire at about 400°, which is about 200° below the temperature required for the ignition of gunpowder, and its combustion is more rapid. In consequence of its whiteness it is not so easily inflamed by a solar lens as gunpowder, unless it is tinged with indigo or carmine, or covered with a little charcoal. Burned in a tube it produces red fumes, having the odor of nitrous acid. When substituted for gunpowder in fire-arms, the extreme suddenness of its explosion is apt to burst the barrel, but it is a powerful projectile agent. For mining purposes it is preferable to gunpowder, in producing less noxious fumes; and it is not deteriorated in damp air, or even (when subsequently dried) by immersion in water; and, weight for weight, its explosive force is between 3 and 4 times greater than that of gunpowder. The extreme rapidity of its combustion is well shown by placing a flock of it upon a small heap of gunpowder, where it may be exploded by a hot wire without kindling the powder. Exclusive of the traces of nitrous acid above adverted to, aqueous vapor, carbonic oxide, carbonic acid, and nitrogen, are the products of its combustion.

Pyroxyline, as above prepared, is insoluble in dilute acids; it dissolves in methylic and acetic ethers, and in acetone. It is very slightly soluble in mixtures of ether and alcohol.

Gun-cotton for medical purposes is prepared by keeping the cotton for about two hours in a mixture of 2 parts of powdered nitre, and 3 of sulphuric acid; after washing and drying, it is digested in a mixture of about 90 parts of ether, and 10 of alcohol. Spread upon silk this solution furnishes a good sticking-plaster.

A solution of potassa dissolves and decomposes gun-cotton; ammonia also dissolves it, and leaves it, on evaporation, in a pulverulent form. Sulphuric acid dissolves pure gun-cotton and is not discolored by it, unless it contains portions of unchanged cotton. It is scarcely affected by cold nitric acid, but, if heated, nitrous acid vapor is evolved; and on adding water, a white inflammable powder falls, which resembles that obtained by a similar process from a nitric solution of starch—called *xyloidine.*

The production of nitrous acid by the combustion of pyroxyline may be shown by exploding a portion on blue litmus-paper, or on starch-paper, impregnated with a solution of iodide of potassium. The former is reddened, and the latter acquires a deep-blue color.

The pyroxyline used in *photography* requires many precautions for its preparation. Its qualities are materially affected by the proportions of the acids; their sp. gr., the temperature of the mixture, and the period of time during which the cotton is immersed. Mr. Nicol recommends the following formula: Ten ounces, by measure, of sulphuric acid (1·840), and 5 ounces, by measure, of nitric acid (1·370), are to be well mixed, and 2 fluid drachms of water added. When the mixture has cooled to about 130°, place in it, tuft by tuft, well pulled out, 5 drachms of clean cotton. Each tuft should be penetrated by the acid, as it is immersed. The cotton should be kept immersed ten minutes, then removed, washed, and dried. If it appear to dissolve while immersed in the acids, this may be prevented by pressing the cotton together with glass rods. We have found this compound to be very soluble in a mixture of alcohol and ether (p. 472). It leaves, on evaporation, a smooth transparent film. It is not very explosive, but completely combustible.

The following is another formula: Powdered nitre, 925 grains, sulphuric acid (1·8), 1389 grains. When the nitre is entirely dissolved in the acid, plunge in, by separate portions, 62 grains of clean cotton. Immerse for ten minutes, then remove and wash the product.

Generally speaking, the longer the cotton is left in the acid mixture, the less soluble it becomes.

The composition of pyroxyline no doubt varies, according to the mode in which it is prepared. There are at least four varieties known. In all cases it must be regarded as the nitrite of an organic base. The formula for photographic cotton is $(C_{24}[H_{16}(NO_4)_4]O_{20})$ (p. 473). It is a substitution-compound in which 4 atoms of hydrogen are replaced by 4 atoms of nitrous acid. According to Pelouze and Frémy (*Chim. Organ.* vol. i. p. 950), the formation of pyroxyline is as follows:—

$$\underbrace{2(C_{12}H_{10}O_{10})}_{\text{Cellulose.}} + 5(NO_5HO) = 10HO + \underbrace{(C_{24}H_{15}O_{15},5NO_5}_{\text{Pyroxyline.}}$$

The composition of cellulose, or pure woody fibre, may be represented as $C_6H_5O_5$: but a higher equivalent is better adapted to its combinations, and its most convenient formula is $C_{24}H_{20}O_{20}$.

LIGNINE WOOD.—The varieties of wood have cellulose, in various degrees of induration, as their basis, with other substances superadded, giving distinct characters to the several varieties of this important product: in some of the hard and white woods, these foreign matters are unimportant; but in others, as in the resinous, colored, and astringent woods and barks, they materially affect their durability and uses.

The average sp. gr. of wood is 1·5, but it generally floats, in consequence of the air it includes, though there are a few woods—such as guaiacum, ebony, and box—which sink in water. Green wood includes from 30 to 40 per cent. of water; in its ordinary state of dryness, it retains about 25 per cent.: but when artificially dried, as when used for fuel, in which case its humidity greatly diminishes its heating powers (*see* p. 95), it should not retain more than 10 or 12 per cent.

The durability of woods depends upon their state of induration, and upon the extraneous matters, such as resin and tannin, which they contain; but by long exposure to air and moisture, they are all more or less liable to decay (*dry rot*) in consequence chiefly of the presence of a nitrogenous matter, which seems to act as a ferment; the attacks of insects and the growth of fungi and lichens also contribute to these changes. This decay may be to a great extent prevented, by imbuing the timber with certain oils, tars, oxides, and salts; and ropes, sailcloth, &c., may be similarly treated. Alum, sulphate, and pyrolignate of iron, sulphate of copper, corrosive sublimate, and chloride of zinc are some of the substances which have been thus applied; they act by *combining* with the wood or fibre; but when large dense pieces of timber are operated on, there is a difficulty in causing them to be permeated by the solution. In some cases this has been effected by placing the wood and preservative liquor in a vessel admitting of being exhausted, so that the interstitial air of the wood has been pumped out, and the metallic solution forced in on restoring the air's pressure. Another mode of effecting a more entire penetration, consists in rendering the natural functions of the tree available: the force with which the sap rises from the roots to the leaves, is well known, and accordingly, if a tree in full leaf be cut through just above the root, and the cut surface immersed in the metallic solution, this will be carried upwards and transmitted even to the smaller branches. Even a hole bored into the body of the tree, or a section into it by a saw, may be resorted to as means of presenting an absorptive surface to which the protective liquor may be applied. It has also been proposed to apply this system to coloring and perfuming woods, by causing them to absorb colored liquors, or metallic solutions, which by reacting upon each other would cause the deposition of colored precipitates; Prussian blue, chromate of lead, tannate of iron, ferrocyanide of copper, and other similar metallic colors, have thus been formed in the ligneous texture, and it has been similarly pervaded by certain essential oils. (BOUCRERIE, *Ann. Ch. et Ph.*, lxxiv. 113.) Silicious solutions, and solutions of certain phosphates, have also been thus employed, with the twofold object of preservation from decay and protection from fire.

Products of the Decay of Wood.—When wood is kept dry, or when submerged in deep water, it is little prone to change. In mummy-cases, in the roofs of some old buildings, in the piles of bridges, and in submerged forests, wood has remained for centuries in good condition; but under the protracted influence of air and moisture it undergoes a series of changes, the rapidity of which, and their concomitant results, depend upon the texture of the wood and the quantity and quality of the foreign matters associated with it; some promoting and others retarding decay; among the former, certain azotized matters are apparently most active. Carbonic acid and water are always evolved during the decay of wood, and a variety of intermediate compounds are among the solid products, more especially, the brown matter found in soils or mould, and to which the terms *geine*, *humus*, and *ulmine*, have been applied. These or analogous compounds are obtained by the action of alkalies upon several organic products, and amongst these upon woods; they are compounds of carbon, hydrogen, and oxygen in various proportions, and may be regarded as so many steps in those processes of decomposition in which wood, by the loss of water and carbonic acid, gradually passes into the modification of coal. These brown extractive matters combine with alkalies, and have been described as *geic acid* ($C_{40}H_{12}O_{14}$), *humic acid* ($C_{40}H_{12}O_{12}$), and *ulmic acid* ($C_{40}H_{14}O_{12}$). The dark brown exudation on the barks of certain trees, and especially of the *elm*, contains a similar substance, combined with potassa, and allied products have been found in the ferruginous deposits of certain mineral waters, and have been termed *Crenic* and *Apocrenic acids*.

COAL.—Pit coal and many of its allied products are obviously of vegetable origin; but the circumstances under which they have been formed, and deposited in their present localities, are very imperfectly understood.

Lignite, as its name imports, generally retains its ligneous structure; sometimes it resembles indurated peat, and contains brown extractive matter and resin. When heated, it exhales a bituminous odor, and burns with a bright flame. It is found in tertiary strata (p. 236).

Bituminous coal constitutes our common fuel; but there are many varieties of it, differing in color and structure, in their manner of burning, and in the quality and quantity of the gas and coke which they yield on distillation (see p. 254). The geological position in which this coal occurs, is between the New and the Old Red Sandstones, forming the *coal-measures.*

Cannel coal and *Parrot coal* are distinguished by their slaty and conchoidal fracture, their clean surface, and by their yielding a large proportion of gas of high illuminating power, and leaving about half their weight of coke. There is a variety of coal intermediate between that which is highly bituminous and the anthracites, called *steam coal* and *Welsh coal:* it burns well, does not cake, gives little smoke, and yields a porous coke. It is a useful fuel for many closed stoves, when the draught is insufficient for the combustion of anthracite.

Anthracite (ἄνθραξ, coal) is more difficult of combustion, yields little volatile matter, and therefore burns without flame. Some of its varieties are very compact, and split into small fragments when heated.

The essential ultimate constituents of coal are carbon and hydrogen; but it also includes oxygen, nitrogen, sulphur, and various mineral matters, constituting the incombustible residue or *ash*, which is chiefly composed of silicious matter and unburnt charcoal, with carbonate of lime and oxide of iron.

100 parts of several varieties of coal, previously dried at 212°, gave the following results. (VAUX, *Journ. Chem. Soc.*, i. 328.)

	Newcastle.	Staffordshire.	Wigan Cannel.	Anthracite.
Carbon	81·41	78·57	80·07	90.89
Hydrogen	5·83	5·23	5·53	3·28
Oxygen	7·89	12·88	8·09	2·97
Nitrogen	2·05	1·84	2·12	0·83
Sulphur	0·75	0.89	1·50	0.91
Ash	2·07	1·03	2·70	1·61
Specific gravity	1·276	1·278	1·276	1·392
Approximate formulæ	$C_{27}H_{11}O_2$	$C_{26}H_{10}O_3$	$C_{26}H_{10}O_2$	$C_{40}H_8O$

Bitumen, Asphalt, Petroleum.—These, and several allied substances, are closely connected with coal, in reference especially to the products of their destructive distillation. Many of the varieties of coal may be regarded as carbonaceous matters impregnated with bitumen, and the *Bituminous Schists* are earthy compounds, chiefly alumino-silicious, similarly impregnated. The bituminous shales of Dorsetshire, and of Bathgate, near Edinburgh, leave little carbonaceous matter, and nothing in the form of *coke*, but from 20 to 25 per cent. of earthy matter or ash. When distilled in close vessels, their volatile products, on the other hand, are very abundant, and vary in character and composition with the temperature to which they are subjected. If rapidly distilled at a high temperature, gases of high illuminating power abound; if at a lower temperature, liquid oily hydrocarbons in great variety are obtained, and among these, paraffine and its congeners.

Asphalt, or *Mineral Pitch*, in its purest form, may be taken as the type of the Bitumens: it occurs on the shores of the Dead Sea (the *Asphaltic Lake*), in Barbadoes and Trinidad, in Albania, and nearly pure at Coxitambo in South America. It formed a leading ingredient in the celebrated Greek fire of the middle ages. Pure asphalt is black, or dark brown, has a slight bituminous odor, a resinous fracture; sp. gr. 1 to 1·1; it softens when heated, and burns with a smoky flame. It is insoluble in water, sparingly so in alcohol, but abundantly in ether and in benzole. Asphalts and bitumens of various degrees of purity, and from various sources, are used in combination with lime, chalk, sand, &c., for pavements and cements. Two of the proximate components of asphalt have been termed *Asphaltene* ($C_{40}H_{32}O_6$) and *Petrolene* ($C_{20}H_{15}$).

Petroleum, Naphtha. *Rock-Oil. Mineral Tar.* ($C_{24}H_{24}$).—Inflammable oily bodies, issuing often in large quantities from fissures in connection with coal strata, and in other localities, have been long known. The purer varieties are nearly colorless, and burn without residuum (*native naphtha*). Others are brown, and leave asphalt when distilled. The Burmese petroleum or naphtha has long been celebrated: it issues from a sandy loam resting upon bituminous shale and coal strata: it is used in lamps, and mixed with earth for fuel. Enormous quantities of rock-oil have been lately imported from the United States and Canada. In the former country, according to Mr. Hunt, the wells are chiefly found in New York, Pennsylvania, and Ohio. Those of Mecca (Ohio) have been sunk from 30 to 200 feet in a sandstone, which is saturated with the oil. Of 200 wells which have been sunk, a dozen or more yield from five to twenty barrels of oil daily. The wells of Pennsylvania vary in depth from 70 to 300 feet, and the petroleum, or rock-oil, is met with throughout. The oil varies considerably in color and thickness. Its sp. gr. is from 0·830 to 0·890. The oil-wells in the United States are for the most part sunk in the sandstones of the Devonian series; but those of western Virginia and southern Ohio rise through the coal-measures which overlie the Devonian strata. In Canada the oil is found in shales and limestones. At one of the Canadian wells the oil rises from a depth of 234 feet at the rate of 25 barrels, or about 1000 gallons, per hour, and much of it is allowed to run to waste from the inadequacy of the supply of barrels, and of the other means to store it. At another well the supply is alleged to have poured forth at the rate of 70,000 gallons a day uninterruptedly, except when the opening was plugged, for several months. A third well exists of similar capacity; and the other wells which require labor or machinery for pumping are innumerable. The American rock-oil may be regarded as a compound of various hydrocarbons boiling at different temperatures, and possessing different degrees of inflammability.

All these mineral oils, when subjected to fractional distillation, yield products more or less resembling those similarly obtained from coal naphtha, and are available for similar commercial purposes.

COAL-TAR, as produced in the gas-factories, is a very complex substance: it is always alkaline, from the presence of ammonia: it contains aniline and numerous other bases, as well as carbolic and acetic acids. When distilled, fetid ammoniacal compounds pass over, and a light oil (*Coal naphtha*), succeeded by small portions of a heavier oil (dead oil), containing a little paraffine, and by naphthaline: the residuary pitch, or asphalt, is used for common black varnishes. By a careful fractional distillation of the rectified naphtha, the following products are obtained—1, An oil of an alliaceous odor, boiling between 150° and 160°; 2, an oil boiling at 170°, identical with *benzole*, $C_{12}H_6$; 3, an oil consisting chiefly of *toluole*, $C_{14}H_8$, boiling at 240°; 4, an oil boiling between 240° and 290°, having the proportions of *Cumole*, $C_{18}H_{12}$; and 5, an oil between 330° and 340, and resembling *Cymole*, $C_{20}H_{14}$ (MANSFIELD, *Quarterly Journ. Chem. Soc.*, i. 252). Naphtha therefore is a mixture of several apparently definite hydrocarbons. Amongst them benzole is the most important.

NAPHTHALINE ($C_{20}H_8$).—This is a white crystalline substance, obtained by subjecting coal-tar to distillation: it passes over after the coal-oils, and is produced when the vapors of coal-tar are passed through a red-hot tube. It may be purified by sublimation with powdered charcoal. Naphthaline has a faint odor, which has been compared to that of the narcissus, and a slightly aromatic taste; its sp. gr. is 1·05; it is unctuous to the touch, and evaporates slowly at common temperatures; it fuses at about 176°, and crystallizes as it cools; it boils at 420°; the sp. gr. of its vapor is 4·5. It burns with a lurid smoky flame. It is insoluble in water, but alcohol, ether, and some of the oils dissolve it readily; it is deposited from its alcoholic solution in lamellar iridescent crystals. The alkalies have no action upon it.

When gently heated with sulphuric acid it produces a red crystalline compound which, saturated with carbonate of baryta, yields insoluble sulphate, and a soluble *sulphonaphthalate of baryta.* The formula of sulphonaphthalic acid is supposed to be $HO,C_{20}H_7S_2O_5$. Naphthaline combines with chlorine, producing two chlorides, $C_{20}H_8Cl_2$, and $C_{20}H_8Cl_4$, the properties and reactions of which have been studied by Laurent: it also combines with bromine. From these chlorides and bromides a numerous series of substitution-compounds have been derived. By the protracted action of nitric acid on naphthaline, *naphthalic* or *pthalic* acid is formed$=(2(HO),C_{16}H_4O_6)$ which when distilled with lime yields benzole and carbonate of lime. This acid is also one of the products of the action of nitric acid on alizarine.

PARANAPHTHALINE.—Under this term Dumas and Laurent (*Ann. Ch. et Ph.* 1. 187) have described a hydrocarbon resembling naphthaline, but yielding a vapor having the density of 6·78. Paranaphthaline is less volatile than naphthaline, and, therefore, when coal-tar is distilled, it is among the latter of its products. According to Reichenbach (*Poggend. Ann.*, xxviii. 484), paranaphthaline is a mixture of naphthaline and paraffine. The term *anthracene* has been applied to paranaphthaline, and it has been represented as $C_{30}H_{12}$.

Among the last portions of the distillation of coal-tar, a yellow crystalline solid is found, fusing at 455°, and insoluble in most liquids; it has been termed *chrysene*, and its formula is said to be $C_{12}H_4$: it is accompanied by a more fusible substance, *pyrene*$=C_{30}H_4$.

BENZOLE ($C_{12}H_6$); *Benzine.* Benzole was first discovered by Faraday, in the products of the destructive distillation of whale-oil; and Mitscherlich obtained it by heating benzoic acid with excess of hydrate of lime; but it is now procured from coal naphtha, the more volatile products of which, when cooled to 32°, deposit it in a solid form. It fuses at 40°, boils at 170°, and burns with a very smoky flame. It is insoluble in water, but soluble in alcohol and in ether; it dissolves fats and oils, and is a useful solvent of wax, caoutchouc, gutta percha, and numerous resins.

When benzole is exposed to sunlight in contact with chlorine, it produces a crystalline *chlorobenzole*, $=C_{12}H_6Cl_6$; and a *bromobenzole*, $=C_{12}H_6Br_6$, may be similarly obtained. With anhydrous sulphuric acid benzole produces a crystallizable compound, which, acted upon by water, yields *sulphobenzide*, $=C_{12}H_5SO_2$, in which therefore an atom of hydrogen is replaced by an atom of sulphurous acid: *sulphobenzolic acid*, $=C_{12}H_5SO_3+HO,SO_3$ is at the same time formed: but amongst these reactions, those with nitric acid are the most interesting. If benzole is gradually added to red fuming acid, gently heated, there is a considerable action, and on diluting the product, a heavy yellow oil separates, which is *nitrobenzole*, $=C_{12}H_5O_4N$; it boils at 415°, and may be distilled without decomposition; it smells like bitter-almond oil, tastes sweet, and is used by perfumers and confectioners under the name of *essence of Mirbane*, or bitter almonds. When an alcoholic solution of nitrobenzole is mixed with caustic potassa, and distilled, a red oily liquid passes over, which deposits crystals of *azobenzole* ($C_{12}H_5N$); the liquid contains *aniline.* By the action of a mixture of nitric and sulphuric acids upon benzole, a crystalline product, *binitrobenzole*, is obtained, $=C_{12}H_4O_8N_2$. In these derivatives of benzole, one and two atoms of its constituent hydrogen are respectively replaced by one and two atoms of NO_4 (p. 520).

CARBOLIC ACID. *Phenol, Phenylic* or *Phenic Acid* ($C_{12}H_6O_2$, $=HO,C_{12}H_5O$).—When those portions of the acid of coal-tar which distil over between 300° and 400°, are mixed with a strong and hot solution of caustic potassa, a crystalline mass is obtained, which is resolved by the action of water into a light oil, and a heavy alkaline liquid; when the latter is neutralized by hydrochloric acid, the impure carbolic acid separates in the form of a light oil: it requires to be distilled off chloride of calcium, exposed to a low temperature, and freed from the remaining liquid. The pure acid forms a colorless deliquescent crystalline mass, which fuses at 95°, and passes into vapor at 370°. It has a smoky odor, an acrid taste, and the antiseptic properties of kreasote. It is much used as a deodorizer. It does not redden litmus, but produces a transient greasy stain upon the paper. Its sp. gr. is 1·062. When heated in a sealed tube with ammonia it yields aniline and water: ($C_{12}H_6O_2+NH_3=C_{12}H_7N+2HO$). When carbolic acid is distilled with perchloride of phosphorus, one of the results is chloride of phenyle ($C_{12}H_5Cl$), a fragrant liquid, boiling at 277°, and a crystallizable phosphate of phenyle is at the same time formed. A numerous class of substitutional phenylic compounds, in which chlorine, bromine, and nitrous acid replace one or more of the hydrogen atoms, has also been formed; they mostly constitute monobasic acids, and many of their salts are of a definite character.

PARAFFINE (CH) (*parum affinis*) was originally discovered by Reichenbach, among the products of the distillation of wood-tar, but it has more recently been abundantly obtained from the oils derived from the distillation of bituminous schists, and other bituminiferous minerals: it exists in large proportion in some petroleums: it is also contained, in small quantities, in common coal-tar. It is a crystalline solid, without taste, smell, or color. It is not greasy; its sp. gr. is about 0·87; it melts at 112°, and may be distilled over unchanged at a higher heat. Its name is derived from its inertness, or want of affinity, for it resists the action of acids, alkalies, chlorine, and potassium; but it unites by fusion with stearine, cetine, wax, and resin, and dissolves in naphtha, benzole, and oil of turpentine: it is soluble in hot ether, but the solution concretes on cooling; it also separates in crystalline flakes from its solution in hot alcohol. The density of its vapor and its true composition have not been satisfactorily determined, but it is a hydrocarbon of the olefiant type. The substances known as *Fossil wax*, and *tallow*, *Ozokerite*, and *Hatchetine*, which occur in the coal-formations, closely resemble paraffine.

The product known as *Paraffine Oil* is one of the associated hydrocarbons contained in the least volatile portions of the bituminous oils. Together with paraffine it is largely obtained from the bituminous schists accompanying the coal-measures at Bathgate, near Edinburgh, and known under the name of Boghead Cannel. This valuable substance yields nearly three-fourths its weight of volatile matters, leaving an aluminous ash, and only about 6 per cent. of carbon. Paraffine has been applied to the manufacture of candles as a substitute for wax, and paraffine oils are burned in lamps and used for greasing machinery.

PYROXANTHINE ($C_{21}H_9O_4$) is a yellow crystalline solid, which was discovered by the late Mr. Scanlan, as a product of the reaction of potassa on wood-spirit. It is insoluble in water, but is dissolved by boiling alcohol. The crystals melt at 291°. Its most remarkable property is that of forming a rich purple compound with strong sulphuric acid, which slowly becomes blue and black.

WOOD TAR. When wood is subjected to destructive distillation as in the process for the manufacture of gunpowder, and of pyroligneous acid, a large quantity of *tar* is among the products, from which, as well as from common *Stockholm tar*, a variety of hydrocarbons and oxyhydrocarbons may be obtained. The processes, by which these are separated and purified, are mostly tedious and complicated; they have been especially described by Reichenbach. Paraffine is amongst them; but he has also discovered several other definite compounds, such as *kreasote*, *eupion*, *kapnomor*, *pittacal*, *picamar*, and *cedriret*.

KREASOTE (κρὲας, *flesh*, σώζω, *to preserve*) appears to be the principal source of the peculiar odor and of the antiseptic and preservative qualities of wood-smoke. When properly purified it is a colorless oily-looking liquid of great refractive and dispersive power, of a penetrating smoky odor and a burning taste: its sp. gr. is about 1·04; it remains fluid at 17°; it burns with a sooty flame; is sparingly soluble in water, and is neutral to test-paper. It dissolves readily in alcohol, ether, benzole, and acetic acid; and forms a crystalline compound with potassa. It coagulates albumen; and a solution of it, containing not more than 1 per cent., preserves meat from putrefaction. The efficacy of crude pyroligneous acid, as a preservative of provisions, and the peculiar smoky flavor which it confers upon them, appear to be due to kreasote. It is an irritant poison when undiluted, but when largely diluted it has been found effectual in checking vomiting, and as an application in toothache for the destruction of the nerve. It appears to be closely related to phenic (carbolic) acid, and the formula $C_{16}H_{10}O_2$ has been assigned to it.

EUPION is a light oil of a peculiar greasy character (εὖ, and πίων, *greasy*) resembling paraffine oil. It has the formula C_5H_6, and is regarded by Frankland as *hydride of amyl*, $C_{10}H_{11}$,H. *Kapnomor* (καπνὸς, *smoke*, μοῖρα *part*) is a pungent oil, sp. gr. 0·9. The formula $C_{20}H_{11}O_2$ has been assigned to it. *Pitacal* is characterized by affording a blue color with baryta-water. *Picamar* appears to be the *bitter* principle of wood tar, and is contained in the heavy oil. *Cedriret* is a crystallizable product, soluble in kreasote, but insoluble in water and alcohol.

PICRIC ACID. *Carbazotic Acid* ($C_{12}H_2(NO_4)_3O,HO$).—This is a solid acid, crystallizing in yellow prisms, of an intensely bitter taste. It may be procured by the reaction of nitric acid at a high temperature on silk, indigo, salicine, aniline, or oil of tar. This oil is now the principal source of the acid. The crystals are deposited from the boiling solution. They require purification. The crystals are not very soluble in water, but they give to the solution a deep yellow color. The solution stains organic matter, and has strong dyeing properties. The acid is more soluble in alcohol and ether. The crystals are decomposed by heat, and, when suddenly heated, with explosion. The *picrate of potassa* is very sparingly soluble in cold water, so that this acid is sometimes used as a test for potassa.

CHAPTER L.

ESSENTIAL OILS. CAMPHOR. RESINS. AMBER. CAOUTCHOUC. GUTTA PERCHA.

ESSENTIAL OILS.

THE essential or volatile oils may be regarded as the odorous principles of vegetables, and are generally obtained by distilling the plant with water, either in its fresh, salted, or dried state. In some cases the oils are pressed out of the cellular structure, as from orange and lemon peel. They are obtained from all parts of plants, though usually most abundant in the leaves and flowers; and they sometimes differ in different parts of the same plant; thus, with regard to the orange-tree, the leaves, flowers, and fruit, each yield a distinct oil. Some of them are so delicate and evanescent as to require a peculiar mode of treatment, such as those of the flowers of jasmine, tuberose, narcissus, mignonette, &c.: these flowers are stratified with layers of cotton, or wool, imbued with some inodorous fixed oil, which absorbs the perfume of the flowers. When the oil is saturated with the essence, it is digested in alcohol, which abstracts the essential from the fixed oil, and an odoriferous *essence* is obtained. Sometimes the cotton is distilled with water or alcohol to separate the odorous essence, but the fragrance is always more or less impaired by these processes. (*See* PIESSE, *On Perfumes.*)

The essential oils are applied to many useful purposes; some in the manufacture of paints and varnishes, some for burning in lamps; others in pharmacy and medicine, and others in perfumery. They are mostly ready formed in the plant, but they are in some cases generated by the action of water upon peculiar principles, as in the production of bitter-almond oil; and there are a few instances of their artificial production, as in that of *oil of spiræ*, by the oxidation of salicine. When fresh and pure, these oils are mostly colorless or nearly so; a few are green or blue, and some after having acquired color, lose it under the influence of light. Their odors resemble those of the plants yielding them, but are less agreeable, partly in consequence of concentration, for they become more pleasant when diffused in the air, or attenuated by solution in some inodorous vehicle. Their odors are also influenced by their chemical relations to air and water: there are some, such as those of turpentine, lemons, and juniper, which, when distilled off quicklime, out of contact of air are nearly inodorous, but which acquire their characteristic odors when spread upon paper.

The sp. gr. of the essential oils fluctuates between 0·840 and 1·100, and when subjected to a careful fractional distillation, they are mostly resolvable into products differing in sp. gr. and in composition; one of which is frequently a *hydrocarbon*, and the other an *oxyhydrocarbon*, which is sometimes concrete, constituting a species of *camphor* (p. 569). The terms *elaioptene* and *stearoptene* have been applied to these liquid and solid products (from ἔλαιον, *oil*, or στέαρ, *fat*, and πτηνὸς, *volatile*). Their boiling points are very variable, and so are the temperatures at which they congeal, these being often dependent upon the relative proportions of their component oils. They are sparingly soluble in water, to which, as in the medicated waters of the *Pharmacopœia*, they communicate odor and flavor; most of them are copiously soluble in absolute alcohol and in ether, and in fixed oils and liquid hydrocarbons. In consequence of the high price of many of these oils, they are sometimes adulterated with alcohol, with fixed oils, or with cheaper essential oils. *Alcohol* may generally be separated by shaking the adulterated oil with water, and its quantity appreciated by the diminution in the bulk of the original oil; it may also be abstracted by fused chloride of calcium. Moreover the pure volatile oils dissolve, for the most part, in the fixed oils, without interfering with their transparency; but when adulterated with alcohol they produce turbidness. The admixture of a *fixed oil* is shown by the greasy stain which remains on evaporating a drop of the oil before the fire, from a piece of blotting-paper: some of the genuine oils leave a stain, but it is rather resinous than greasy, and admits of being written upon with a pen and ink, or removed by alcohol; the feel of the oil between the finger and thumb is also greasy, and when it is distilled with water, the fixed oil remains in the retort. The adulteration of a *high priced* with a *cheap* essential oil is often difficult of detection, and requires experience in the odor and qualities of the genuine article. When oil of turpentine is so used, its characteristic odor is often covered, until the adulterated oil is dissolved in a little alcohol, and water, added, when the odor and flavor of the turpentine are manifest. The taste of the oil in these cases is often a good guide; oil of lemons is frequently adulterated with turpentine, but its taste is very different from that of the genuine oil. The difference between the indices of refraction of the adulterated and genuine oils has been proposed as a means of detecting falsifications, and Dr. Wollaston suggested an instrument for the purpose (*Phil. Trans.*, 1802); but the refractive power of the genuine oil varies too much to render this method satisfactorily available.

The action of chlorine, bromine, and iodine upon the essential oils, gives rise to an infinity of new compounds, resulting from the substitution of one or more atoms of these elements, for a corresponding number of the hydrogen atoms of the oil; and in some cases, direct combinations ensue. With some of them iodine causes fulmination. Nitric acid acts violently upon most of them; they are more quietly decomposed by sulphuric acid. They are not saponifiable by the alkalies. When their vapors are passed over heated potassa, or soda, hydrogen is sometimes evolved, and an acid compound with the base is formed.

For the purpose of chemical description, the essential oils may be arranged under three divisions; 1. Those composed of carbon and hydrogen; 2. of carbon, hydrogen, and oxygen; 3. those containing sulphur.

1. HYDROCARBONS.—The elementary composition of this group may be represented by C_5H_4: it includes many isomeric compounds of which *oil of turpentine* may be assumed as the type. *Oil of turpentine* $C_{20}H_{16}$ (*camphene; camphyle*), is obtained by distilling the turpentine of commerce, with water. There are many varieties of turpentine; but that principally resorted to as a source of the oil, is derived from different species of *pinus*, and chiefly imported from North America. The first product is purified by redistillation. The original turpentine is thus resolved into the volatile oil, and into residuary resin; which, when retaining a portion of water, is known as *yellow rosin;* or, as *colophony*, after fusion at a higher temperature.

Oil of turpentine, or *turps*, as the common oil is usually called, is a colorless and very mobile liquid; sp. gr. 0·865, boiling at 312°, and yielding a vapor of the density of 4·764 (p. 517). It has a characteristic odor, a hot pungent taste, and burns with a large sooty flame: it is almost insoluble in water, but soluble to some extent in alcohol and in ether. Under the name of *Camphene* it was at one time largely used as a source of light, and when carefully burned in a properly constructed lamp, gives a brilliant light; but if the oil is not fresh, and has been exposed to air, it clogs the wick, and smokes. Its use has lately been superseded by *rock-oil* and other modifications of naphtha.

When oil of turpentine which has been agitated with water is kept for some time at a temperature of 120°, it deposits crystals$=C_{20}H_{16}+HO$. When the oil and water are left together at common temperatures, another hydrate, $=C_{20}H_{16},6HO$, is produced. A crystalline compound of hydrochloric acid and oil of turpentine has long been known under the name of *artificial camphor*$=C_{20}H_{16}+HCl$. Corresponding hydrobromates and hydriodates have also been formed. The decomposition of these, and other terebinthic compounds, has led to the discovery of several isomeric hydrocarbons, principally distinguished by their action on polarized light, some causing left-handed and others right-handed rotation of the ray. Oil of turpentine is a great solvent of ozone. When exposed to air it absorbs oxygen and acquires some of the properties of ozone. Thus it will bleach organic colors (p. 103).

The oils of *lemon, bergamot, orange, juniper*, and many others, are isomeric with turpentine oil.

2. OXYHYDROCARBONS.—The *essential oils containing oxygen* are very numerous, and include *Camphor* and its modifications. *Bitter-almond oil* and *Spiræa oil* are elsewhere noticed, and there are others which have been the subjects of minute investigation. Some of these, when distilled, are separable into a more volatile hydrocarbon and a less volatile oxyhydrocarbon, but the nomenclature applied to these compounds is often confused and unsatisfactory; in some cases a hydrocarbon, and in others an oxyhydrocarbon, having been assumed as the radical of the series.

Oil of Cumin, for instance, may be resolved into a hydrocarbon$=C_{20}H_{14}$, which has been called *Cymol*, and an oxyhydrocarbon$=C_{20}H_{12}O_2$ called *Cuminol.* But cuminol has also been represented by the formula $C_{20}H_{11}O_2+H$, and has been described as a *hydride* of a radical called *Cumyle* $C_{20}H_{11}O_2$. *Oil of Aniseed* is similarly separable into a hydrocarbon, isomeric with oil of turpentine, and an oxyhydrocarbon (the concrete portion of the oil), $C_{20}H_{12}O_2$; but this is sometimes represented as containing a radical$=C_{16}H_7O_4$, to which the term *anisyl* has been applied, and from which a voluminous series of substitution and other compounds has been obtained.

Analogous radicals or bases have been obtained from many of the other essential oils, or have been assumed as existing in them; and it has often been found convenient in theory, to represent the oils as hydrides of these radicals; thus, *oil of cinnamon* is represented as a hydride of *cinnamyl,* by the formula $C_{18}H_7O_2+H$, another of its products, *cinnamic acid,* being $C_{18}H_8O_2+O$.

CAMPHOR ($C_{20}H_{16}O_2$).—Common camphor is the produce of the *Laurus Camphora* of Japan, China, and Java. It is extracted, by distillation with water, from the roots and wood of the tree, and refined by sublimation. It is tough, white, translucent, of a peculiar odor and flavor, and evaporates at ordinary temperatures, gradually subliming in close vessels, and attaching itself, in hexahedral and prismatic crystals, to the surface most exposed to light. Its sp. gr. is 0·987 to 0·996; but after long immersion in water, this is so affected by changes of temperature, that this substance floats on water above 50°, but sinks at a lower temperature. It fuses at 370°, and boils at 400°, when it may be distilled without decomposition. When a clean fragment is placed upon water, it acquires a peculiar rotatory motion: it requires about 1000 parts of water for solution, but is very soluble in alcohol, ether, chloroform, acetone, acetic acid, and sulphide of carbon. It burns with a white smoky flame.

By the protracted action of hot nitric acid camphor is converted into *camphoric acid,* $C_{20}H_{16}O_8$ or $2(HO)C_{20}H_{14}O_6$, which crystallizes in acicular prisms, rendered anhydrous by sublimation, and sparingly soluble in water.

A variety of camphor known as *Borneo camphor,* the produce of the *Dryabalanops Camphora,* contains two equivalents more of hydrogen than common camphor: it is associated with a hydrocarbon (Borneen)$=C_{20}H_{16}$, identical, therefore, with oil of turpentine. Camphor is contained in several of the essential oils; and substances resembling it are found in the *Inula Helenium,* in *Assarabacca,* and in some of the *Anemones.*

3. ESSENTIAL OILS CONTAINING SULPHUR.—There are several essential oils which contain nitrogen and sulphur, amongst which the oil of black mustard-seed, garlic, assafœtida, and horseradish are the most remarkable.

Oil of Black Mustard-seed.—To obtain this oil, the cake of the seed, after the fixed oil has been expressed, is made into a paste with water, which after some hours is subjected to distillation, in the same way as bitter-almond oil is distilled from the almond-cake. As, in that case, the oil is formed by the action of emulsine upon amygdaline in the presence of water, so in this instance, the volatile and pungent mustard-oil is formed by the action of a substance analogous to emulsine, which has been termed *myrosine,* upon a peculiar substance existing in the black mustard-seed, and which has been termed *myronic ccid, sulphosinapisine,* and *sinapine.* The oil which first passes over, when dehydrated by means of fused chloride of calcium, is an acrid, colorless liquid, soluble in alcohol and ether: it boils at 290°, and the density of its vapor is 3·44. Its ultimate elements are $C_8H_5NS_2$; so that it has been regarded as the sulphocyanide of a hydrocarbon, $=C_6H_5$, to which the term *Allyl* has been applied, and which has been isolated by the action of sodium upon iodide of allyl (C_6H_5I). This iodide, under the name of *iodized propylene,* was obtained by Berthelot (*Ann. Ch. et Ph.*, xliii. 257) as a result of the action of biniodide of phosphorus upon glycerine: it has been assumed as the basis of numerous derivatives, included in what has been termed the *allyle series.*

Oil of Garlic is a fetid sulphuretted product, which appears to consist of oxide and sulphide of allyle ($C_6H_5O+C_6H_5S$), both of which have been isolated.

Resins.

These substances are found as proximate constituents of many plants: those which have been principally examined are such as either flow naturally from fissures in the bark or wood, or are obtained from incisions in the trees and shrubs which produce them. They are almost always in the first instance mixed with variable proportions of essential oil, which either evaporates on exposure to air, or becomes resinified by the action of oxygen. Mixtures of essential oil with resin are called *balsams*. The *gum resins* are natural mixtures of gum and resin.

Resins when pure are inodorous; a few of them are crystallizable; they are usually pale yellow or brown; and they become electric by friction. The greater number of them are heavier than, and insoluble in water, and have little taste. They are generally softened, or even fused, when boiled in water. In the air they melt and burn with a sooty flame. They are thus distinguished from gums. When subjected to dry distillation, they yield resin-oil, volatile liquids, and inflammable gases.

Many of the natural resins are mixtures of two or more resinous substances, separable by the action of alcohol. There are many of them which, when in alcoholic solution, redden litmus, and combine with alkalies; others are indifferent, and some have been regarded as basic.

Gum resins are variable in composition, and often include volatile oils: they are not entirely soluble either in alcohol or in water, but form milky mixtures with the latter.

There are a few of the resins, and their allied substances, which require especial notice.

Colophony; Common rosin.—This is the residue of the distillation of turpentine (p. 568). It is brittle, tasteless, of a smooth shining *resinous* fracture; sp. gr. 1·080; softens at about 180°, and fuses at 275°. According to Unverdorben, it includes two distinct acid resins, which he designates *pinic acid*, and *silvic acid*, the former preponderating. As respects the composition of these acids, it appears that they are *isomeric*, and have the formula ascribed to colophony ($C_{40}H_{29}O_3,HO$).

Silvic acid is obtained by mixing an alcoholic solution of colophony with an alcoholic solution of oxide of copper, drying the precipitate, and digesting it in alcohol, which dissolves the silvate, but leaves the pinate of copper. Sulphuric acid is added to the alcoholic solution, and it is then precipitated by water, which throws down silvic acid, and which, dissolved in alcohol, yields crystals on evaporation.

Pinic Acid.—When pinate of copper is dissolved in boiling alcohol acidulated by hydrochloric acid, and water is added to the mixture, pinic acid is precipitated, in the form of a colorless resin. This substance is not crystallizable, but in other respects resembles. silvic acid. The *pinates* are less soluble in ether than the silvates, and *pinate of magnesia* is insoluble in alcohol, whereas the *silvate* is soluble.

When colophony is heated somewhat above its point of fusion it acquires a dark color, and is less easily soluble in alcohol: in this state it has been called *colopholic acid.* Distilled over an open fire, colophony is resolved into carbon, water, and *colophene;* there is also formed a liquid hydrocarbon $=C_{10}H_8$, having the properties of *terebene.* But these products vary with the mode of distillation, for Frémy represents them as consisting of water, together with a thick yellow oil, which he terms *resinéine*, and represents as $=C_{40}H_{28}O_2$; and by distilling in the same way, a mixture of 1 part of resin and 8 of powdered quicklime, he obtained two liquids, which he calls *resinone*, $=C_{10}H_9O$, and *resinéone*, $=C_{29}H_{23}O$, carbonic acid being at the same time formed.

A resin isomeric with colophony is obtained from the turpentine of the *pinus maritima*, and has been distinguished as *pimaric acid.* All these resins readily combine with the alkalies, and enter largely into the composition of common yellow soaps.

Elemi, Anime, Sandarac, or juniper resin, and *Mastic,* each contain two distinct resins, separable to a great extent by the alternate action of cold and hot alcohol, and differing slightly in composition (JOHNSTON, *Phil. Trans.*, 1840). *Guaiacum* is a greenish resin, which gives a gray powder, becoming green by exposure to air, and acquiring a fine but transient blue by the action of nitrous ether. Aqueous chlorine renders guaiacum green, blue, and brown. Paper imbued with tincture of guaiacum becomes blue in the more refrangible spectral rays, but reverts to greenish yellow in the less refrangible rays. It is used for a test for ozone.

Copal, the resin of the *Hymenæa verrucosa,* is characterized by its difficult solubility in alcohol; but when powdered and exposed for some months to the air, it becomes more soluble. It is the basis of some excellent varnishes, and is generally fused before it is dissolved in oils or spirit. *Lac* is also a valuable ingredient of varnishes, rendering them, like copal, tough and durable: its secretion appears to depend upon the puncture of a small insect (the *Coccus ficus*), made for the purpose of depositing its ova, upon the branches of several plants growing chiefly in India, more especially the *Ficus Indica, Ficus religiosa,* and *Rhamnus Jujuba.* The twig soon becomes incrusted with a dark reddish substance, constituting *stick-lac,* which, when washed and coarsely pulverized, forms *seed-lac;* and this, formed into thin plates by fusion, is called *shell-lac;* it consists of about 90 per cent. of a peculiar resin, which appears to be a mixture of three or four distinct resinous products. Lac is an important ingredient in varnishes and *lacquers,* and is largely used in the manufacture of hats, and of sealing-wax.

Red sealing-wax is made by carefully fusing a mixture of 48 parts of shell-lac, 19 of Venice turpentine, and 1 of Peru balsam, to which 32 parts of finely-levigated cinnabar and some sulphate of lime are afterwards added. In the cheaper kinds of red sealing-wax, red lead is substituted for vermilion, and there is a large addition of common rosin, which causes the wax to run into thin drops when fused. *Black sealing-wax* is made of 60 parts of shell-lac, 10 of Venice turpentine, and 8 of finely levigated ivory-black.

Varnishes.—The principal substances used in varnishes as solvents are the oils of nuts, linseed, and turpentine, as well as alcohol, ether, chloroform, and benzole. The solids employed are amber, copal, mastic, sandarac, lac, anime, benzoin, and colophony. They are sometimes colored with various vegetable coloring principles.

Asphaltum is an ingredient in *Japan* or *black varnish,* and caoutchouc in those which are required to be elastic and waterproof. The best photographic varnish is a solution of amber in chloroform. The characters of a good varnish are, that it should firmly adhere to the surface to which it is applied, that it should not change color or lose lustre, by exposure to light and air; and that it should not be long in drying. Varnishes are distinguished as *spirit* and *oil varnishes;* the former are the most brilliant, but most brittle, the best spirit varnishes being those containing lac or copal. The article known as *French polish* is an alcoholic solution of shell-lac, a little linseed oil being added at the time of its application: it is laid on by a ball of cotton-wool, and then rapidly rubbed in the direction of the fibres of the wood: it is ultimately finished off, after drying, by friction with tripoli and oil. The varnishes prepared with oil of turpentine, are less brittle than those in which alcohol only is used.

AMBER.—This substance, usually regarded as a fossil resin, is chiefly brought from the Southern coast of the Baltic, where it is thrown up on the beach; it is found on the coast of Norfolk; it also occurs in beds of brown coal. It is generally of a peculiar yellow color, transparent or translucent, slightly heavier than water, and becoming electric by friction. It is only soluble to a small extent in alcohol and in ether. Subjected to dry distillation it fuses, giving off water, oily matters, and succinic acid; the latter derived apparently from the decomposition of that portion of resin which is soluble in ether; and the oils, from the insoluble and apparently bituminous part. Sixteen ounces of amber, carefully distilled, yield about an ounce of impure acid, three ounces of oil, and ten of a torrefied resin, fit for the preparation of varnish.

Succinic acid, $2(HO),C_8H_4O_6$, is a product of the action of nitric upon stearic acid. It is also formed by fermentation, from asparagine, and from malic acid. It crystallizes in rhombic plates, soluble in five parts of cold, and two of boiling water; it may be obtained anhydrous, by distillation with anhydrous phosphoric acid; if the crystals are heated to 450°, they lose a portion of their water, and a monohydrated acid sublimes. The succinic, is a very stable acid; it resists the action of chlorine and of boiling nitric acid. When fused with caustic potassa it yields oxalic acid, and an inflammable gas. The soluble *succinates* produce a bulky reddish-brown precipitate in the neutral and basic salts of peroxide of iron, and they have been used as a means of separating it from oxide of manganese. When heated with bisulphate of potassa, they give a sublimate of succinic acid.

SUBERIC ACID, $C_{16}H_{12}O_6$, is one of the products of the action of nitric acid on oleic acid (p. 577); it was originally produced by the action of nitric acid upon cork. When pure, it is a difficultly soluble crystalline powder; *suberates* of the alkaline bases are soluble; they give white precipitates with the salts of lead and silver, $=2(MO,)C_{16}H_{12}O_6$.

CAOUTCHOUC (*Indian Rubber, Gum Elastic*), was first brought to this country at the beginning of the last century, moulded into the shape of bottles and animals, and used for rubbing out pencil marks: it has since been applied to a variety of important purposes, and many tons of it are annually imported from South America and the East Indies. The trees which yield it are the *Jatropha* and *Urceola elastica*, and several others, and it is found in small proportion in the poppy, lettuce, euphorbium, and other plants having a viscid milky sap. The fresh juice of the tree is a yellow, milky fluid, which, when exposed to warm air, forms an elastic deposit, retaining albumen and other impurities which are found in the commercial article. This is frequently of a dark color, and has a sp. gr. varying from 0·926 to 0·960. Pure caoutchouc is a hydrocarbon, being, according to Faraday, C_8H_7, although other authorities give it C_5H_4; thus making it isomeric with oil of turpentine. The remarkable elasticity of this substance, and its chemical peculiarities, have led to a multitude of important applications of it in the industrial arts. (HANCOCK *on Caoutchouc*, &c.: MUSPRATT'S *Chemistry*, Art. *Caoutchouc*, &c.)

In its ordinary state it becomes hard at low temperatures, but never brittle; it is soft and very elastic when warmed; and when heated to about 260°, melts into a viscid mass, which never regains its former characters. It burns with a smoky flame and exhales a peculiar odor. Subjected to destructive distillation, it affords a mixture of various hydrocarbons, gaseous and liquid; the latter, under the name of *Caoutchine* $C_{20}H_{16}$, having a peculiarly penetrating, greasy, and disagreeable odor. Caoutchouc is insoluble in water, alcohol, dilute acids, and alkalies. Ether, chloroform, bisulphide of carbon, rectified oil of turpentine, benzole, coal-naphtha, and some other hydrocarbons, soften and dissolve it; some of these solvents leaving it on evaporation in its elastic condition. In this dissolved state, it is extensively used for water-proofing and other purposes. The processes by which the commercial caoutchouc is purified, kneaded, moulded into blocks, cut into sheets, ribbons, and thread, are almost exclusively mechanical, but are necessary preliminaries to its most important applications, many of which are dependent upon a process which has been termed *Vulcanization*, and which consists in subjecting it, by heat or solution, to the action of sulphur. By this process it becomes so far modified as to resist the action of its ordinary solvents, and of the greasy oils, and to retain perfect pliancy and elasticity at the low temperatures which harden, and at the high temperatures which soften common India rubber. When a sheet of rubber is immersed in melted sulphur, it absorbs a portion of it, without any material change; but if heated in this sulphurized state, to about 300°, the vulcanization is effected. So also if sulphur is added to the solution of the rubber in turpentine or naphtha, it retains it ordinary properties after the evaporation of these solvents, until heated to the vulcanizing temperature (270° to 300°). Sulphur is sometimes imparted to rubber by dipping it in thin sheets into a solution of chloride of sulphur. A hard compound of sulphur and rubber is called *Ebonite.*

The cause of the change effected by vulcanization is not well understood; but it is generally supposed that the rubber retains about two per cent. of sulphur in chemical combination, inasmuch as all beyond that quantity may be removed by appropriate solvents. It has also been surmised that the process of vulcanization has conferred an *allotropic* condition upon the rubber, and that the whole of the sulphur may be withdrawn, still leaving it in its altered condition (p. 54). The removal of sulphur is effected on the large scale, by boiling the vulcanized rubber in a solution of sulphite of potassa. A large quantity of silicate of magnesia, in fine powder, is sometimes incorporated with the rubber before vulcanization, to give it a smooth and non-adherent surface. An article known as *marine glue* is made by dissolving a mixture of caoutchouc and shell-lac in coal-naphtha: it is of extreme adhesiveness.

GUTTA PERCHA, in composition and in its general chemical characters, is closely allied to caoutchouc: it was first brought into notice in 1846, and has now become an important article of commerce: it is the produce of the *Isonandra percha*, a forest tree abounding in the islands of the Eastern Archipelago. It is a tough, unyielding, fibrous substance, generally met with in black or brown masses. When immersed in boiling water, it softens, and admits of moulding into any requisite shape, but hardens again on cooling. It becomes powerfully electric by friction, and is an excellent insulator. It is applied to a variety of useful and ornamental purposes, in many of which it is advantageously substituted for leather.

Gutta percha consists of a distinct principle, *gutta*, associated with two resinous compounds. The gutta is represented by the formula $C_{40}H_{32}$, and is a pure hydrocarbon. The resins have the same formula, with an addition of two and four atoms of oxygen respectively.

CHAPTER LI.

FATS AND FIXED OILS. PRODUCTS OF THEIR DECOMPOSITION. SPERMACETI. WAX. SOAPS.

Fats and Fixed Oils.

These substances are common to animals and vegetables; they vary in consistence from thin oil (olive oil) to hard fat (suet). When pure, they are neutral; they leave a greasy spot upon paper, which does not disappear when moderately heated. They are insoluble in water, but more or less soluble in alcohol and ether, and are insipid and inodorous. In vegetables they chiefly occur in the seed, and pericarp of the fruit (olive), and are generally obtained by pressure, with or without the aid of heat. In animals, the adipose cells are easily ruptured by heat, which liquefies and expands the fat, so that it runs out and collects upon the water in which the crude fat is boiled. The melting points of oils and fats vary from about 20° to 140°. At high temperatures (500° to 600°) they do not distil unchanged but evolve acrid products, and are resolved, at a red heat, into inflammable gases and vapors, of high illuminating power. Their specific gravity, which is below that of water, varies much with temperature: the sp. gr. for instance, of hog's lard at 60° is 0·938; in its fluid state at 122° it is 0·892; at 155° it is 0·881; and at 200°, 0·863. Some of these oils are little affected by exposure to air, but gradually become rancid; others absorb oxygen, and form a resinous varnish; they are known as *drying oils;* and when their surface is much extended, as in greasy rags and cotton-waste, this change is sometimes attended by spontaneous combustion. The drying quality of these oils is generally increased by heating them with oxide of lead or manganese.

When the solid fats are subjected to pressure between folds of bibulous paper, they afford more or less of fluid oil; and when the liquid oils are cooled to about 32°, they deposit more or less of a concrete matter. The liquid portion is termed *oleine* or *elaine* (ἔλαιον, *oil*), and the solid, *stearine* (στέαρ, *fat*), with which a variable portion of *margarine* (μάργαρον a pearl, from its pearly lustre) is associated, each of these being compounds of a distinct *fatty acid,* with a sweet principle, *glycerine* (γλυκύς *sweet*). These acids are the *oleic,* the *stearic,* and the *margaric;* so that oleine is an oleate, stearine a stearate, and margarine a margarate, of glycerine. Besides these, many fats contain distinct volatile acids, such as *butyric, capric,* and *caproic acids,* in butter; *hircic acid* in goat's fat, *phocenic acid* in fish-oil, &c. Oleine may be more or less separated from stearine by ether or oil of turpentine, in which liquids it is much more soluble than stearine.

In the process of *saponification,* the fatty bodies are heated with hydrated alkalies, generally with soda, by which they are decomposed, the glycerine is set free, and *oleates, stearates,* and *margarates* of the alkaline bases are formed.

$$\text{Fat or oil} \quad . \quad . \quad . \quad . \left\{ \begin{array}{ll} \text{Stearine} & \left\{ \begin{array}{l} \text{Stearic acid} \\ \text{Glycerine} \end{array} \right. \\ \text{Margarine} & \left\{ \begin{array}{l} \text{Margaric acid} \\ \text{Glycerine} \end{array} \right. \\ \text{Oleine} & \left\{ \begin{array}{l} \text{Oleic acid} \\ \text{Glycerine} \end{array} \right. \end{array} \right.$$

These combinations (soaps) are in their turn decomposed by the greater number of other acids, and the fatty acids are separated. These acids are insoluble in water, but soluble in alcohol and in ether, and are less fusible than the original fats. They are soluble in oil of turpentine and in benzole, and when free from volatile products, are insipid and inodorous. The soaps of alkalies are soluble, but those of the alkaline earths, and of most of the other metallic oxides, are insoluble in water; hence it is that *hard waters* are unfit for washing, in consequence of the earthy salts which they contain, and which give rise to the production of insoluble soaps.

Stearine ($C_{114}H_{110}O_{12}$) (*Stearate of Glycerine*) is best obtained from mutton suet, by boiling it in ether, and filtering the hot solution; as it cools, it deposits stearine, which, after having been pressed in bibulous paper, may be purified by a second solution, and crystallization. Its fusing point is about 140°. It is insoluble in water, but soluble in boiling alcohol and ether, which, however, deposit nearly the whole of it as they cool.

Stearic Acid ($HO,C_{36}H_{35}O_3$).—When stearine is saponified, it is resolved into stearic acid and glycerine, a change which has been represented by the following equation:—

$$\underbrace{C_{114}H_{110}O_{12}}_{\text{Stearine.}} + 6HO, = \underbrace{C_6H_8O_6}_{\text{Glycerine.}} + \underbrace{3(HO,C_{35}H_{35}O_3)}_{\text{Stearic acid.}}$$

The acid may be obtained by decomposing a soluble stearine soap by tartaric acid, and purifying the product by solution in boiling alcohol, from which it separates in crystalline flakes: it may be further purified by solution in ether. It is white, inodorous, and tasteless, but it reddens litmus: it fuses at about 160°, and may be distilled *in vacuo*, but when highly heated in the air it undergoes more or less change. Stearic acid may be distinguished from stearine by its ready solubility in a boiling solution of potassa.

Stearates.—Stearic acid forms monobasic and bibasic salts (neutral and acid). The stearates of the alkalies are soluble in water, alcohol, and ether; but when the aqueous solutions of the neutral compounds are largely diluted, they deposit flakes of the acid stearate. The stearates of the alkaline earths may be obtained by double decomposition, from bistearate of potassa: they are insoluble. Stearate of potassa is the basis of *soft soap*, and stearate of soda of the principal *hard soaps:* these stearates are separated from their solutions in water by excess of alkali, and also by chloride of sodium and some other salts. Stearate of lead is the basis of lead-plaster.

Margarine ($C_{108}H_{104}O_{12}$) (*Margarate of Glycerine*).—This substance is found in some animal fats, but it is best obtained from olive oil, by cooling it to 32°, pressing out the oleine, and dissolving the residue in boiling alcohol, from which the margarine separates in pearly crystals. It is resolved by the alkaline bases into glycerine and margaric acid.

Margaric Acid ($HO,C_{34}H_{33}O_3$) is obtained by decomposing the soap of olive-oil and potassa, by acetate of lead or chloride of calcium: an insoluble margarate and oleate of lead or lime is formed, from which the oleate may be abstracted by cold ether; the remaining margarate may then be decomposed by dilute hydrochloric or nitric acid, when the margaric acid separates, and may be purified by crystallization from its alcoholic solution:

it fuses at about 140° ; in other respects it resemble stearic acid, and the *margarates* closely resemble the stearates.

According to Heintz, margarine is a mixture of stearine and *palmitine* (found in *palm-oil*), and consequently margaric acid is a mixture of stearic and palmitic acids.

Oleine ($C_{114}H_{104}O_{12}$) (*Oleate of Glycerine*).—Oleine is the principal ingredient in the fat-oils which remain fluid at common temperatures. It is procured by separating the margarine and stearine from a fat oil, by cold and pressure, dissolving the liquid portion in ether, evaporating, and digesting the residue in cold alcohol, which dissolves the oleine, and leaves margarine and stearine undissolved. Oleine is colorless, inodorous, and tasteless ; its sp. gr. is about 0·9. It is insoluble in water, but abundantly soluble in alcohol and in ether. It remains fluid at 32°.

Oleic Acid ($C_{36}H_{33}O_3$) is obtained by saponifying almond-oil with potassa, and decomposing the soap by hydrochloric acid, which separates a mixture of oleic and margaric acids : this, by digestion with oxide of lead, is converted into oleate and margarate of lead, and by digesting these in ether, an acid oleate of lead is dissolved. The ethereal solution is mixed with its bulk of water and decomposed by hydrochloric acid, which throws down chloride of lead, and leaves the oleic acid in solution, from which it is obtained by evaporation. The crude oleic acid, produced by pressure in the manufacture of stearine candles, may be similarly purified.

Oleic acid is colorless, concretes at about 50°, and reddens litmus ; it is insoluble in water, but abundantly soluble in alcohol. The neutral oleates have little tendency to crystallize. The soluble alkaline oleates are soft fusible compounds, more soluble in alcohol than in water, and are decomposed by excess of water, into free alkali, and acid compounds.

GLYCERINE ($C_6H_8O_6$) (γλυκὺς, *sweet*).—This substance was discovered by Scheele. It is obtained by boiling hydrated oxide of lead with olive oil and water : the solution thus formed, freed from lead by sulphuretted hydrogen, filtered, evaporated to the consistency of syrup, and then exposed *in vacuo* over sulphuric acid until it no longer loses weight, leaves the glycerine. It is now produced in large quantities by soap and candle-makers, and has been applied to many useful purposes in medicine and the arts.

Glycerine is an uncrystallizable, colorless, neutral, inodorous liquid, of a sweet taste, sp. gr. 1·28, soluble in all proportions in water and in alcohol, but nearly insoluble in ether. It does not dry by exposure to air. It dissolves baryta, lime, oxide of lead, and many salts. When mixed with a solution of caustic potassa, it readily dissolves hydrated oxide of copper, forming a deep blue solution, which, however, produces no suboxide when boiled. When boiled with a solution of potassa, no glucic acid is produced, and the liquid does not become dark-colored like glucose under similar circumstances. Sulphuric acid does not carbonize it in the cold : it is thus distinguished from sucrose. When heated in a retort, part passes over and part is decomposed, producing the pungent vapors of *acrolein ;* but it may be distilled without decomposition in a current of superheated steam, at a temperature between 400° and 500°. It is not susceptible of vinous fermentation, but when left for some months in a warm place, mixed with a little yeast, it produces *propionic acid.* Impure glycerine digested with alcohol produces butyric ether. Distilled with dilute sulphuric acid and peroxide of manganese, it yields carbonic and formic acids. Mixed with twice its weight of sulphuric acid there is considerable elevation of temperature, and after the mixture has cooled, if it be diluted, saturated by milk of lime, and filtered, it yields, on evaporation, crystals of a salt of lime containing *sulphoglyceric acid*, $=C_6H_5O_7+2SO_3$. A corresponding *Phosphoglyceric acid* is said to exist in the brain, and in yelk of egg.

In combination with the fatty acids, glycerine produces the various fats and oils, but they appear to combine in various proportions: assuming stearic acid as $C_{36}H_{35}O_3$, stearine will be a terstearate of glycerine:—

$$\underbrace{C_6H_7O_5}_{\text{Glycerine.}} + \underbrace{3(C_{36}H_{35}O_3)}_{\text{Stearic acid.}} = \underbrace{C_{114}H_{112}O_{14}}_{\text{Stearine.}}$$

and oleine a teroleate of glycerine:—

$$\underbrace{C_6H_7O_5}_{\text{Glycerine.}} + \underbrace{3(C_{36}H_{33}O_3)}_{\text{Oleic acid.}} = \underbrace{C_{114}H_{106}O_{14}}_{\text{Oleine.}}$$

and so with regard to other fatty acids. Berthelot has synthetically reproduced the fats by the union of their acids with glycerine, and has pointed out the existence of analogous combinations, in which 1 and 2 equivalents of the respective acids are similarly combined with glycerine, producing distinct fatty bodies (*Ann. Ch. et Ph.* 3ème sér. xli. p. 216).

Nitric acid decomposes glycerine, and among the products, are oxalic and carbonic acids. When glycerine is dropped into equal parts of strong nitric and sulphuric acids, a heavy oily-looking liquid is formed, which is called *nitroglycerine.* It is powerfully explosive, and is said to possess strongly poisonous properties. It has been sometimes called *Glonoine.* It is a substitution-compound, in which 2 atoms of hydrogen are replaced by 2 atoms of nitrous acid. Its formula is therefore $(C_6H_6(NO_4)_2O_6)$.

Action of Sulphuric Acid on Fats and Oils.—This acid generally so combines with the proximate principles of the fatty bodies, as to form a series of distinct acid products, such as *sulphostearic*, *sulphomargaric*, and *sulpholeic acids;* the glycerine at the same time yielding *sulphoglyceric acid;* but when sulphuric acid is heated with the fatty bodies, the glycerine is decomposed, and the fatty acids are set free. This process is resorted to upon the large scale, for the production of the fatty acids for the manufacture of candles. The tallow is mixed with about a sixth part of oil of vitriol in large copper vessels, and subjected to a temperature of about 350°, by means of highly heated steam; sulphurous and carbonic acids are abundantly evolved, in consequence of the action of the sulphuric acid upon the glycerine. The liberated fatty acids, after having been well washed, are distilled in a current of steam, heated to between 500° and 600° by transmision through a red-hot pipe; the fatty acids are carried over, leaving their impurities in the form of a black residue, and are then subjected to pressure so as to squeeze out the more fluid oleic portions, and leave the stearic acid in a fit condition for candle-making. But the decomposition of the fats by highly heated steam only, has lately been carried to such perfection, as not only to yield the fatty acids, but also the glycerine, in a very pure state, a process which will probably entirely supersede that by sulphuric acid.

Action of Nitric Acid on Fats and Oils.—These products may be divided into two classes: 1. Those which are volatile, and pass over in distillation; and 2. Those which are comparatively fixed, and remain in the retort; they are as follows:—

Volatile acids.	*Volatile acids.*	*Fixed acids.*
Formic	Œnanthylic	Succinic
Acetic	Caprylic	Adipic
Butyric	Pelargonic	Pimelic
Valeric	Capric	Suberic
Caproic		Sebacic

These products are obtained by gradully dropping oleic acid into a retort containing nitric acid, heated to about 130°: violent action ensues, and the distillate consists of water holding the most volatile and soluble acids in solution, such as formic, acetic, and butyric, covered by an oily layer of the valeric and other acids. On pouring off the oil, agitating it with baryta-water, and submitting the solution to successive crystallizations, caproate of baryta is first obtained—then œnanthylate, caprylate, pelargonate, and caprate, and, lastly, valerate. The more fixed acids are dissolved in water, and the solution saturated with carbonate of soda: on evaporation, crystals of acetate of soda separate, and on adding sulphuric acid to the mother-liquor, an oily layer, consisting of butyric and metacetonic acids is formed. (Regnault.) There are other modes of obtaining these and the other fixed acids, which are elsewhere noticed.

Butyric Acid ($C_8H_7O_3,HO$).—Butter includes several fatty bodies (*see* Milk), amongst which are butyrin, caproin, and caprylin, to which its peculiar smell and taste have been referred: these may be resolved by saponification into glycerine, and butyric, caproic, and caprylic acids. Butyric acid, obtained by the decomposition of butyrate of lime by hydrochloric acid, is a volatile oily body, sp. gr. 0·963, and boiling at 315°: it has the odor of rancid butter, a pungent taste, and is soluble in water, alcohol, and ether: its salts are mostly soluble and crystallizable. It is among the products of the action of nitric acid upon olein, and of certain oxidizing agents upon fibrin or casein, and is found in some fruits. The readiest mode of obtaining it is that of Pelouze and Gélis, and is as follows: a solution of sugar of the sp. gr. 1·064, is mixed with powdered chalk amounting to half the weight of the sugar, and to this a portion of casein or curd is added, equal to 8 or 10 parts for every 100 of sugar, and the mixture kept at a temperature of about 80°; viscous and lactic fermentations ensue, carbonic acid and hydrogen are evolved, and after some weeks *butyrate of lime* is formed in the liquor: in this case the lactic acid which is first formed, passes, by loss of carbonic acid and hydrogen, into butyric acid.

$$\underbrace{2(HO),C_{12}H_{10}O_{10}}_{\text{Lactic acid.}} = \underbrace{HO,C_8H_7O_3}_{\text{Butyric acid.}} + 4CO_2+4H$$

Capric Acid ($C_{20}H_{19}O_3,HO$) is among the products of the action of nitric acid on oleine, and is one of the results of the saponification of butter, but it is most readily procured by the oxidation of the *oil of Rue* by nitric acid (Gerhardt), and has hence been termed *Rutic acid.* It is obtained pure by the decomposition of caprate of baryta by sulphuric acid: it forms acicular crystals fusible at 86°, of a sour acrid taste, and goat-like odor.

Caprylic Acid ($HO,C_{16}H_{15}O_3$) is liquid at temperatures above 60°, little soluble in water, boils at 258°, and has a nauseous odor.

Caproic Acid ($HO,C_{12}H_{11}O_3$) is a liquid of a sour odor and taste, boiling at 390°, and sparingly soluble in water.

Valeric Acid ($HO,C_{10}H_9O_3$).—The volatile oil, obtained by distilling the root of *valerian* with water, is a mixture of a hydrocarbon $=C_{10}H_3$, with an oxygenated oil convertible into valeric acid. This acid has also been obtained from angelica root, and from the berries and bark of the Guelder-rose (*Viburnum opulus*): it is an occasional product of the oxidation of fatty bodies, and is artificially produced by the action of oxidizing agents on amylic alcohol (*fusel-oil*). It is a colorless liquid, smelling strongly of valerian, and of a sour pungent taste. It boils at 270°, and the density of its vapor is 3·55. It is soluble in about 30 parts of water, but may contain 20 per cent. of water without losing its oily appearance. The *Valerates*, when pure and dry, are nearly inodorous, but generally have a valerianic odor and sweetish taste; they smell strongly of valerian when moistened with a dilute acid; some of them have been used medicinally. Acted upon by chlorine, valeric acid furnishes two compounds in which 3 and 4 atoms of its hydrogen are replaced by chlorine, the *chlorovalerisic* and *chlorovalerosic* acids; and by the protracted action of nitric acid, a part of it is converted into *nitrovaleric acid*, $=HO,C_{10}H_8O_7N$.

FIXED VEGETABLE OILS.

In adverting to the general nature and properties of the oils and fats, we may select a few for more special notice; taking linseed-oil as a specimen of the *drying oils*, olive-oil of the non-drying or *greasy oils*, and palm-oil of the *concrete oils* or *vegetable butters*.

The drying oils, when exposed to air, gradually assume resinous characters, by the absorption of oxygen: the greasy and concrete oils become rancid, principally in consequence of mucilaginous and albuminous impurities which gradually react upon them; they boil and are decomposed at about 650°.

Linseed oil, obtained by expression from the seeds of the *Linum usitatissimum*, or *common flax*, remains fluid until cooled down to about 0°, when it gradually solidifies. It is largely used for paints and varnishes, and for these purposes its drying quality is increased by heating it with a little litharge. It is an important component of *Printers' Ink*, for which it is first heated and then set fire to, and allowed to burn for some time, when it is extinguished, and the heating continued till a film forms upon it; in this state it is called *varnish*, and is easily miscible with fresh oil, or with turpentine, or other matters required for thinning or tempering it, and about a sixth or eighth part of fine lamp-black is then added. Silk and leather are varnished and enamelled with similar preparations of linseed-oil. *Walnut*, *hemp*, and *poppy-oil* also rank with the drying oils, but are inferior to linseed-oil.

Olive-oil, expressed from the fleshy part of the olive, varies in quality according to the mode of obtaining it. What is termed *virgin-oil* is obtained by gentle pressure at common temperatures: it has a very slight nutty flavor, and is long in becoming rancid. Its sp. gr. at 60° is about 0·915: it congeals at about 36°. This oil is unrivalled for culinary use, and being less apt than most other oils to thicken by exposure to air, it is preferred for greasing delicate machinery, especially watch and clock-work. In order to prepare it for this purpose, the finest and purest cold-drawn oil is first selected: it is then cooled, and the more liquid portion poured off from the fatty deposit; a piece of sheet lead or some shot are then immersed in it, and it is exposed in a corked phial to sunshine; a white matter separates, after which the oil becomes clear and colorless, and is poured off for use.

Almond-oil is prepared from sweet and bitter almonds; the purest is cold-drawn, by gentle pressure, from coarsely-powdered almonds: when hot-pressed, it has a deeper color, and becomes sooner rancid.

Colza oil is an inodorous yellowish oil obtained from cabbage-seed (*Brassico oleifera*). It has a sp. gr. of ·915.

Oil of Ben, from the seeds of the *Moringa aspera*, separates soon after expression into oleine and margarine; the former is much esteemed for oiling watch-work, as it neither becomes viscid nor rancid; hence also its excellence for certain scented oils, as of jasmine and tuberose flowers.

Castor-oil is obtained from the seeds of the *Ricinus communis*. This is the heaviest of the fixed oils, its sp. gr. being 0·969. It is a thick, viscid, colorless oil; when cooled to 0° it congeals into a transparent mass. Although not a drying oil, it hardens by exposure to air. It dissolves in all proportions of alcohol and ether, and thus differs from other fixed oils. It forms a thick tenacious mass when mixed with collodion. It is used as a hair-oil, and medicinally as a mild aperient. The products of its saponification are peculiar; and when acted on by nitrous acid it produces a concrete fatty substance, the *palmic* or *ricinelaidic acid.*

In the subjoined table we have given the specific gravities of good samples of the principal fixed oils:—

Sperm oil	.8750	Southern whale	·9225
Colza	·9156	Poppy	·9254
Olive (flask)	·9158	Cod-liver	·9285
Olive (jar)	·9171	Linseed	·9362
Olive (cask)	·9174	" boiled	·9506
Almond	·9214	Castor	·9674

Palm-oil and *Cocoa-nut oil* are good specimens of *vegetable butters. Palm-oil* is chiefly produced from the fruit of the *Elais Guineensis;* it is orange-colored, but admits of bleaching, and has the violet odor of orris-root. It is used in the manufacture of soap, candles, and of a composition for greasing axles of railway carriages. *Cocoa-nut oil,* from the *Cocos nucifera,* fuses at about 70° ; but its stearine, mixed with a portion of the stearic acid of tallow, forms a good and cheap candle. By saponification it affords several distinct acids. *Chocolate-nut oil,* expressed from the seed of the *Theobroma Cacao,* gives greasiness to *Chocolate,* which is made by torrefying the bean, and grinding it into a fine paste in a hot mill or mortar. The varieties of cocoa are derived from the same source. *Nutmeg butter,* the concrete oil of the nutmeg, and *Laurel-oil,* the fat of the bay berry, belong also to this class, and when saponified yield *myristic* and *lauric acids,* and glycerine.

ANIMAL FATS are generally contained in the adipose membrane or cellular tissue, which is chopped up and heated so as to liquefy the fat: the remaining membranes are rendered crisp by the heat, and when the fat has been pressed out of them are sold in the form of flat cakes, called *greaves* or *cracklings,* used as a coarse food for dogs, as a manure, and in the manufacture of ferrocyanide of potassium. *Whale oil,* when saponified, yields fatty acids and glycerine, and traces of *phocenic acid. Spermaceti-oil* deposits the peculiar white fatty crystalline matter, *Spermaceti.* The oil itself is an oleate of glycerine. It is the lightest of the fixed oils, having a sp. gr. of 0·878. It is of a yellow color, and when cooled to about 45° assumes a semi-solid state. Spermaceti, or *Cetine,* when saponified, affords no glycerine, but in its place a distinct base termed *Ethal,* $=C_{32}H_{34}O_2$. Pure spermaceti ($C_{64}H_{64}O_4$), fuses at about 120°; its sp. gr. is 0·940; it dissolves in boiling anhydrous alcohol and in ether, but falls on cooling. When subjected to destructive distillation it is resolved into a liquid hydrocarbon, *cetene,* $=C_{32}H_{32}$, and *ethalic* or *palmitic acid* ($C_{32}H_{31}O_3HO$,). *Ethal* fuses at about 118°, and is deposited from its hot alcoholic solution in white flakes. When distilled with anhydrous phosphoric acid it yields *cetene.* When oxidized by the protracted action of boiling nitric acid, spermaceti yields succinic, œnanthylic, pimelic, and adipic acids.

Bees'-wax consists, according to Brodie (*Phil. Trans.,* 1847–49), of three substances separable by boiling alcohol: namely, of *Myricin* ($C_{92}H_{92}O_4$), which is insoluble; *Cerin* ($C_{54}H_{54}O_4$), which is deposited in crystals as the solution cools; and *Cerolein,* which is retained in solution. Their relative proportions vary, but in ordinary bees'-wax there appears to be about 73 per cent. of myricin, 22 of cerin, and 5 of cerolein. The *Myrica cerifera,* and some other trees, yield *vegetable wax.*

SOAPS.

Common *hard soaps* are chiefly made with tallow and soda, they are therefore stearates, margarates, and oleates of soda. The sp. gr. of the solution of caustic soda is about 1·15, and is prepared in the usual way by the action of lime upon carbonate of soda. When the lye is raised to its boiling-point the tallow is gradually added so long as the lye saponifies it, and in this way a liquid is obtained, which holds the soap and glycerine in solution: to separate the former, common salt is added; soap being insoluble in brine, is thus brought to float upon the surface, and, if the brine is concentrated, the soap separates nearly in an anhydrous state; but as this is not the object of the manufacturer, the quantity of salt employed is only such as to effect the separation of the soap without dehydrating it. New soap is said to contain about 50 per cent. of water, and to retain above 30 per cent. when comparatively hard and dry. There is, therefore, a manifest advantage to the consumer in purchasing dry and old soap, while the object of the vendor is to sell the soap as humid as possible, and to prevent its desiccation, which is effected by keeping it in damp cellars. Soap is sometimes colored, mottled, or marbled, by the addition of coloring matters: the mottling is produced by oxide of manganese. Sometimes a solution of sulphate of iron is used, which being decomposed, causes the diffusion of oxide of iron through the soap; in these cases the mottling is originally black, but becomes red or brown upon the exterior of the bars in consequence of the action of the air. A considerable quantity of common rosin is added to the yellow soaps of commerce. There are also other additions made to soap, some of which are supposed to improve its detergent quality; but, generally speaking, they deteriorate the article, and are principally resorted to as adding to the weight of the soap by the substitution of cheap materials; sand, clay, fuller's earth, alkaline silicates, sulphate of soda, Cornish clay, starch, flour, and many other substances, have been employed.

The soaps known in commerce as *Spanish soap* and *Marseilles soap* are soda-soaps of olive-oil. Palm-oil and cocoa-nut oil are also largely used as sources of soap, and mixtures of these with the animal fats and bone-grease are employed as the basis of scented and other toilet-soaps.

The soaps of potassa are distinguished from those of soda by remaining *soft*. Common soft soap is frequently made with fish-oil. *Naples soap* is a perfumed potassa-soap made with lard. *Transparent soap* is obtained by dissolving soap in alcohol, which is afterwards distilled off, so as to leave a soft brown transparent residue, which is dried in moulds or balls.

When the fats and oils are decomposed by oxide of lead, the resulting combinations of the fatty acids with that oxide, is known under the name of *Lead plaster*. (*Emplastrum plumbi; Diachylon.*)

ACROLEINE ($C_6H_4O_2$).—When the ordinary fatty bodies are subjected to destructive distillation, the oleic acid is partially converted into sebacic acid, the stearic into margaric acid, and the glycerine into acroleine. When glycerine is distilled with anhydrous phosphoric acid, water and acroleine are the products, and the latter may be dehydrated by rectification over chloride of calcium. Pure acroleine is a limpid colorless liquid, of a highly irritating odor, lighter than water, boiling at about 125°, and burning with a bright flame; it is soluble in alcohol and ether, but only sparingly so in water. It soon undergoes spontaneous changes, depositing an isomeric white substance, *disacryle*, and a resinoid body; and when exposed to air, or more especially when oxidized by oxide of silver, it is converted into *acrylic acid*=($HO,C_6H_3O_3$), a portion of the oxide being at the same time reduced: $C_6H_4O_2+3AgO,=(AgO,C_6H_3O_3)+2Ag+HO$.

CHAPTER LII.

VEGETABLE ACIDS.

The acids of the vegetable kingdom are very numerous as a class. About 170 are now known. They are for the most part solid and colorless, and many are crystalline. They are combined with potassa, soda, or lime, and are thus contained as salts in the juices of plants. Some are educts, *i. e.*, they exist in the vegetable structure, and are separated by simple processes. The tartaric, citric, malic, gallic, and tannic acids, are instances of this class. Others, like the pyrogallic, mucic, and picric acids, are products of art. These are the most numerous, and their number is annually increasing. Others, again, as the oxalic and benzoic acids, are both educts and products.

The vegetable acids are soluble in water and in alcohol: they form with bases, various classes of well-defined crystalline salts. By reason of their superior affinity, they sometimes displace mineral acids from their saline combinations. Thus oxalic acid separates lime, and the oxides of silver and copper, from the solutions of the salts of these bases; and picric acid separates potassa from the salts of that alkali. Tannic acid precipitates the salts of lead, antimony, and other metals. This acid generally forms precipitates (insoluble compounds) with most of the alkaloids, and separates them from their mineral acid combinations. Some of these acids have a simple constitution, being formed of three elements COH : one (the oxalic acid) is formed of CO only. Others, especially those of artificial origin, are much more complex : thus picric, or carbazotic acid, has the composition of ($C_{12}H_2O(NO_4)_3,HO$). When dissolved in water, some, such as the tartaric citric, and gallic acids, undergo decomposition, and vegetable mould results. Others, such as the oxalic, show no tendency to decomposition. All are decomposed by heat in close vessels : some are volatile when heated to a moderate temperature in air (benzoic, formic, acetic); others are fixed, and are decomposed when strongly heated, either being entirely burnt, or leaving a residue of carbon. When the salts of these acids are heated in close vessels, carbon and a carbonate of the base result. The equivalents of these acids are high: they are easily determined by the rules already explained (p. 515).

TARTARIC ACID ($C_8H_4O_{10}2HO=\overline{T}$).

This acid is found free, and in combination, in many vegetables : its principal source is the juice of the grape, in which it exists in the form of *tartar*, or bitartrate of potassa ($KO,HO,C_8H_4O_{10}$). This salt is decomposed as follows : 4 parts of it in fine powder, are well mixed with 1 part of powdered chalk, and the mixture thrown, by small portions at a time, into 10 parts of boiling water; when the effervescence is over, the whole is stirred and left to subside ; the liquid, which is a solution of neutral tartrate of potassa, is then poured off the sediment, which is tartrate of lime, and a solution of chloride of calcium is added to it. This throws down an additional portion of tartrate of lime, which is mixed with the first, and having been well washed, is decomposed by dilute sulphuric acid ; this forms sulphate of lime, while the tartaric acid remains in solution, and is obtained by slow evaporation. The first crystals require to be redissolved, and digested with a little purified animal charcoal until the liquid is colorless; it is then again evaporated and crystallized. Tartar may be similarly decomposed by carbonate of baryta and chloride of barium; the resulting sulphate of baryta falls more rapidly than the sulphate of lime, and may be used for white paint.

Crystallized tartaric acid is very sour: its sp. gr. is 1·74; it is translucent, and of complicated forms, derived from an oblique rhombic prism. It acquires electric polarity by heat. It is permanent in a dry atmosphere: water dissolves about 1·5 its weight at 60°, and more than twice its weight at 212°. It is also soluble in alcohol. The dilute aqueous solution soon becomes mouldy. It is converted into oxalic and acetic acids by fusion with potassa.

$$\underbrace{[C_8H_4O_{10},2HO]}_{\text{Tartaric acid.}} + \underbrace{3\,[KO,HO]}_{\text{Potassa.}} = \underbrace{[KO,C_4H_3O_3]}_{\text{Acetate of potassa.}} + \underbrace{2[KO,C_2O_3]}_{\text{Oxalate of potassa.}} + \underbrace{6[HO]}_{\text{Water.}}$$

It is transformed by the action of peroxide of manganese, or of lead, into formic and carbonic acids.

$$\underbrace{[C_8H_4O_{10},2HO]}_{\text{Tartaric acid.}} + \underbrace{6[PbO_2]}_{\text{Peroxide of lead.}} = \underbrace{2[PbO,C_2HO_3]}_{\text{Formate of lead.}} + \underbrace{4[PbO,CO_2]}_{\text{Carb. of lead.}} + \underbrace{4[HO]}_{\text{Water.}}$$

Tartaric acid is distinguished by the white granular precipitate which it produces when added in excess to solutions containing potassa. If these solutions are very dilute, the crystalline precipitation is accelerated by the addition of alcohol. It produces a white precipitate, soluble in an excess of the acid, in lime, baryta, and strontia-water, and in acetate of lead. It is used in calico-printing, and is much employed as a cheap substitute for citric acid in lemonade and in effervescent solutions. In the laboratory it is used as a test for the salts of potassa, and to prevent the precipitation of certain oxides, as the oxide of antimony, and titanic acid.

The tartaric acid of commerce is apt to be contaminated by traces of sulphuric acid and of lead. To detect sulphuric acid, chloride of barium may be used: if added in excess, or if the solution of tartaric acid is concentrated, tartrate of baryta will fall; but the presence of sulphuric acid in the precipitate is recognized by its insolubility in hydrochloric acid, which acid dissolves tartrate of baryta. Sulphuretted hydrogen is the test for the presence of lead.

Pasteur has shown that there are two modifications of crystallized tartaric acid. The crystals of one variety, when dissolved in water, turn the polarized ray to the right—*dextro-tartaric*, or the common tartaric acid. Other crystals selected from the same mass, when dissolved in water, turn the ray to the left—*lævo-tartaric acid.* Both sets of crystals are unsymmetrical, but the absence of symmetry is exactly in opposite directions. It is remarkable that when equal parts of the two acids are mixed, crystals are deposited from the mixture, which appear to be identical in properties with racemic acid: they have no action on a ray of polarized light. As racemic acid differs in chemical properties from the tartaric, these facts show a singular relation between the crystalline forms and the chemical and optical properties of bodies.

The *tartrates* are mostly crystallizable, and are either neutral or acid. In the neutral tartrates 2 atoms of base are combined with 1 atom of acid, as in neutral tartrate of potassa, which is $2(KO),C_8H_4O_{10}$, or in tartrate of potassa and soda $=KO,NaO,C_8H_4O_{10}$. In the acid tartrates (or bitartrates) 1 atom of water replaces 1 of the bases, as in bitartrate of potassa, which is KO,

$HO,C_8H_4O_{10}$. There is also an important class of tartrates in which one of the bases is a protoxide and the other a teroxide, the salt being neutral, as in the tartrate of potassa and antimony (emetic tartar), which is $KO,SbO_3,C_8H_4O_{10}$. Lastly, there are tartrates in which one of the bases is replaced by a weak acid, as in the boro-tartrate of potassa $=KO,BO_3,C_8H_4O_{10}$.

Tartrate of potassa, $2(KO),\overline{T}$, used as an aperient under the name of *soluble tartar*, forms prismatic crystals of a saline and bitter taste, soluble in two parts of water. Most of the acids occasion a precipitate of the acid tartrate in the aqueous solution of this salt, by abstracting an atom of potassa.

Acid Tartrate. Bitartrate of Potassa. Tartar $(KO,HO,\overline{T})$.—This salt exists in the juice of the grape, and is deposited in wine-casks in the form of a white or red crystalline incrustation, called *argol*, or *crude tartar*. It is purified by dissolving it in boiling water, with one-twentieth of its weight of pipeclay, which absorbs the coloring matter, and falls as a sediment, the crystals of tartar separating afterwards upon the surface of the liquor, and upon the sides and bottom of the boiler; the term *cream of tartar* was originally applied to the imperfectly crystallized superficial crust.

The acid tartrate of potassa is also formed by adding excess of tartaric acid to a solution of potassa: the mixture presently deposits crystalline grains, and furnishes an example of diminution of solubility by increase of acid in the salt. Upon this the use of tartaric acid as a *test* for potassa depends; for soda forms an easily soluble supertartrate, and affords no precipitate.

The crystals of this salt, which are rhombic prisms, include one equivalent of water, which is not separable at a heat much below that at which the acid of the salt begins to be decomposed. They are hard, gritty, and subacid; sp. gr. 1·95. This salt is soluble in 184 parts of water at 68°; and in 18 parts at 212°. It is rendered much more soluble by the addition of boracic acid or of borax; 2 parts of borax and 5 of tartar are soluble in about six times their weight of boiling water; on evaporating the solution, the residue concretes into *Le Fevre's soluble cream of tartar*, or *sal-gummosum*. When exposed to heat in a close vessel, tartar fuses, blackens, and is decomposed, and carbonate of potassa, mixed with charcoal (*black flux*) remains. It is an excellent flux in the reduction of metallic ores, upon a small scale, its alkali promoting their fusion, and the carbonaceous matter tending to reduce the oxides. Tartar is sometimes adulterated with pounded quartz or calcareous spar; the former is detected by its insolubility, the latter by effervescence with dilute hydrochloric acid. Tartrate of lime is often present in purified tartar; it separates in tufts of acicular crystals from a hot solution of the salt.

Tartrate of soda $(2(NaO),\overline{T}+4HO)$ forms acicular crystals, soluble in about their own weight of water. When their aqueous solution is mixed with half their weight of tartaric acid, it yields small prismatic crystals of *acid tartrate of soda*, $=NaO,HO,\overline{T},2HO$, of an acid taste, soluble in 8 parts of cold and 1·8 of boiling water. Tartrate of soda is formed extemporaneously by dissolving equal parts of powdered tartaric acid and of bicarbonate of soda, in separate portions of water, and then mixing the solutions; it forms a refreshing saline and slightly aperient draught.

Tartrate of potassa and soda $(KO,NaO,\overline{T}+8HO)$ is prepared by saturating the excess of acid in tartar, with carbonate of soda: it is the *Soda tartarizata* of pharmacy; it forms fine transparent prismatic crystals. This salt has long been used as a mild aperient, under the name of *Rochelle Salt*, and *Sel de Seignette*, having been first prepared at Rochelle by an apothecary of the name of Seignette. The crystals are soluble in about 3 parts of cold water.

Tartrate of lime is often found as a crystalline deposit in light white wines. It falls on dropping tartaric acid into lime-water, and is soluble in excess of the acid.

Tartrates of iron.—The prototartrate falls as a whitish crystalline powder on adding tartaric acid to protosulphate of iron. When recently prepared and moist peroxide of iron is dissolved in tartaric acid, an uncrystallizable salt is produced, which is not precipitated by the alkalies.

A *pertartrate of iron and potassa* is formed by digesting hydrated peroxide of iron with tartar and water: made into balls, and dried, it forms the *globuli martiales*, or *Boules de Nancy*, of old pharmacy.

Tartrate of copper forms a bluish green crystalline precipitate in a mixture of tartrate of soda and sulphate of copper: if the solutions are very dilute, the salt is long in falling, but on striking the glass, or drawing lines upon it with a glass rod, it soon appears. Dissolved in a solution of soda, this salt forms a deep blue liquid, useful as a test for grape-sugar (p. 528).

Tartrate of lead is a white crystalline powder thrown down by tartaric acid, or a tartrate, from a solution of nitrate of lead. After having been heated in a glass tube to dull redness, it leaves a pyrophorus, which inflames when shaken out into the air, in consequence of the rapid oxidizement of the finely-divided lead.

Tartrate of potassa and antimony; Emetic tartar ($KO,SbO_3,C_8H_4O_{10},HO$), is obtained by boiling any of the forms of SbO_3 with tartar and water. It is a white salt, of a nauseous styptic taste, slightly efflorescent, soluble in about 14 parts of cold, and in less than 2 parts of boiling water. Its solution is rendered turbid by hydrochloric, nitric, and sulphuric acids, but not by the fixed alkalies: the fixed alkaline carbonates, and lime-water, decompose it. Ammonia throws down oxide of antimony, especially when aided by heat. Infusion of galls and many other vegetable bitter and astringent infusions form a precipitate in a solution of emetic tartar, which is generally said to be inactive, and hence decoction of bark has been recommended as an antidote to its poisonous effects. Solution of sulphuretted hydrogen only precipitates strong solutions of emetic tartar; weaker solutions are merely reddened by it: it is also decomposed by hydrosulphate of ammonia: in these cases the precipitate is *sulphide of antimony.* Heated to redness, out of the contact of air, it furnishes a highly-pyrophoric residue, which contains an alloy of potassium and antimony.

Action of Heat on Tartaric Acid.—When common crystallized tartaric acid is heated to about 350°, it fuses without losing weight, and congeals on cooling into a vitreous mass, which has the same saturating power as the original acid, but which produces salts differing in crystalline form, and more soluble than the common tartrates. If the heat exceed 360°, the acid becomes monobasic, but still without loss of weight, and is represented by $C_8H_5O_{11},HO$: it forms with potassa an uncrystallizable, deliquescent salt. These isomeric modifications have been designated *metatartaric* and *isotartaric* acids: when solutions of their salts are boiled, they gradually revert to common tartrates. When the common acid is kept in fusion at about 372°, it loses half an equivalent of water, and is changed into *tartralic acid.* The *tartralates* are quite distinct from the tartrates: those of lime, baryta, and strontia, are soluble in water, and there is no difficultly soluble potassa salt.

When the temperature of the fused tartaric acid is raised to 392° it loses an equivalent of water, and becomes *tartrelic acid:* in this state it forms a peculiar syrupy precipitate with the acetates of lime, baryta, and strontia, and produces neutral salts with one equivalent of base. The tartralates are converted into tartrates, when boiled with water.

By carefully continuing the action of heat on tartaric acid, it may be obtained *anhydrous;* it is then white, amorphous, and insoluble in cold water: but by the protracted action of water, or by boiling, it reverts to its ordinary condition, by the resumption of two atoms of water.

Characters of Tartaric Acid.—1. When heated on platinum foil, it melts and burns with a reddish flame, evolving a peculiar odor. It leaves a slight residue of carbon. 2. Its aqueous solution is precipitated by lime-water, the white precipitate (tartrate of lime) being dissolved by a slight excess of acid, or by a large quantity of water. 3. A concentrated solution of the acid is precipitated by a solution of potassa, provided the acid is in excess. A small quantity of alcohol facilitates the precipitation. 4. Nitrate of silver produces no precipitate in a diluted solution. When the acid is neutralized by potassa, nitrate of silver throws down a white precipitate, which is blackened and decomposed when heated to 212°. 5. A few drops of the acid solution evaporated on a glass-slide, leave prismatic crystals, which assume a plumose form.

RACEMIC ACID: *Uvic Acid; Paratartaric Acid.*—This acid, formerly considered as peculiar to the grapes of certain districts, has been found generally in the juice of sour grapes. It is obtained by saturating the juice with carbonate of soda: the double tartrate is allowed to crystallize, and the double racemate, being more soluble, remains in the mother-liquor; it is decomposed by carbonate of lime, and the racemate of lime (treated as the tartrate) affords crystals of racemic acid, in the form of oblique rhombic prisms. It may be obtained anhydrous; and in this state, as also in the intermediate states of hydration, it resembles tartaric acid, but it is distinguished by its inferior solubility in alcohol, and by furnishing a precipitate with nitrate and sulphate of lime, as well as with chloride of calcium.

The relations of the anhydrous tartaric acid to its several hydrated modifications, are as follows:—

Anhydrous tartaric acid	$C_8H_4O_{10}$
Crystallized tartaric acid	$C_8H_4O_{10}$ 2HO
Metatartaric acid	$C_8H_4O_{10}$ 2HO
Isotartaric acid	$C_8H_5O_{11}$ HO
Tartralic acid	$2(C_8H_4O_{10})3HO$
Tartrelic acid	$C_8H_4O_{10}$ HO
Racemic acid	$C_8H_4O_{10}$ 2HO

PYRUVIC ACID; *Pyrotartaric Acid.*—When tartaric acid is subjected to distillation at about 400°, it furnishes, among other products, a liquid and a crystalline acid. The former produces a characteristic red color with protosalts of iron, and is monobasic: its formula is $HO,C_6H_3O_5$. The latter is bibasic: it forms soluble salts with baryta, strontia, and lime: its formula is $2(HO),C_{10}H_6O_6$.

CITRIC ACID ($C_{12}H_5O_{11},3HO=\overline{Ci}$).

This acid, discovered by Scheele in 1784, is found in several fruits, but is especially abundant in lemon-juice. To obtain it, the juice, clarified by heating it with a little white of egg, is saturated with chalk added in small portions, so long as it occasions effervescence: this throws down citrate of lime; but a portion of acid citrate remains dissolved, which may be neutralized by hydrate of lime. When the liquid no longer reddens litmus, the precipitated citrate is washed, and decomposed by dilute sulphuric acid, which forms sulphate of lime, and the citric acid is retained in solution; it it filtered off and evaporated until a crystalline pellicle appears on the surface:

crystals of citric acid are deposited, which are purified by repeated solution and crystallization. (The practical details of the process are given in Parkes' *Chemical Essays.*) A gallon of good lemon-juice yields about 10 ounces of the pure acid. Citric acid crystallizes in rhomboidal prisms, which are dissolved by their weight of cold water, and are soluble in alcohol, but not in ether. It is considered as tribasic, the formula of the ordinary citrates being $3(MO),C_{12}H_5O_{11}$. The ordinary crystals deposited from a hot saturated solution are $3(HO),C_{12}H_5O_{11}+HO$; but those obtained from spontaneous evaporation, from a cold solution, are $3(HO),C_{12}H_5O_{11}+2HO$. The former neither lose weight nor transparency at 212°, but the latter, dried at 212°, lose their adventitious water, and become $3(HO),C_{12}H_5O_{11}$. Anhydrous citric acid has not been isolated. When the crystals are highly heated, inflammable gas and vapor are disengaged, and a yellow residue obtained which is *aconitic acid.* Citric acid is used in the preparation of acid drinks, and in pharmacy, as a substitute for lemon-juice. When mixed with tartaric acid, the adulteration may be detected by adding to the acid, dissolved in cold water, a solution of acetate of potassa, which occasions the precipitation of acid tartrate of potassa. When citric acid is added to lime-water, the liquid remains clear until heated: it then becomes turbid, and deposits citrate of lime. This character distinguishes it from several other vegetable acids. Heated with sulphuric acid, citric acid is resolved into carbonic oxide, carbonic acid, acetic acid, and water. The action of sulphuric acid on this acid and tartaric acid is different. When tartaric acid is heated with sulphuric, the mixture is intensely blackened; when citric acid is thus treated, the liquid acquires only a pale-yellow color. The presence of tartaric acid would be indicated by a considerable darkening. Decomposed by fusion with caustic potassa, it yields oxalic and acetic acids, and water.

Citrates.—The citric, like other tribasic acids, forms neutral and acid salts: they are mostly soluble in water, and when lime-water is added to their solutions, they become turbid when boiled, but again clear on cooling. The citrates of potassa and of soda are used medicinally. Citrate of lime is the usual source of the pure acid.

Action of Heat on Citric Acid.—When carefully heated, citric acid loses 2 atoms of water, and is transformed into *aconitic acid* (equisetic or citricic acid), an acid found in the varieties of aconite, and in the equisetums:—

$$\overbrace{3HO,C_{12}H_5O_{11}}^{\text{Citric acid.}} = \overbrace{C_{12}H_6O_{12}}^{\text{Aconitic acid.}} + 2HO$$

Under the continued influence of heat, the aconitic acid yields carbonic acid, and an oily distillate which crystallizes on cooling, and is a mixture of two isomeric acids, one much less soluble than the other, the *itaconic* (pyrocitric or citricic acid), and the *citraconic acid;* their formula is $2HO,C_{10}H_4O_6$.

$$\overbrace{C_{12}H_6O_{12}}^{\text{Aconitic acid.}} = \overbrace{C_{10}H_6O_8}^{\text{Itaconic acid.}} + 2CO_2$$

Characters of Citric Acid.—1. When heated on platinum, it melts, and burns with a yellow flame, leaving scarcely any carbon. 2. Its aqueous solution is not readily precipitated by lime-water until it is boiled, when citrate of lime is thrown down. 3. A concentrated solution of the acid is not precipitated by potassa. On this is founded a method of detecting the adulteration of citric with tartaric acid. Cover a glass plate with a layer of solution of potassa, and drop on the liquid the powdered acid. If pure, the citric acid simply dissolves: if tartaric acid is present, stellated prisms of acid tartrate of potassa are formed in groups, and remain. 4. Nitrate of silver produces in the solution, no precipitate. When the acid is neutralized by potassa, nitrate of silver throws down white citrate of silver, which is only slightly discolored and partially decomposed when heated to 112°. 5. A few drops of the acid evaporated slowly on a glass slide, leave small circular groups of prismatic crystals radiating from a centre.

MALIC ACID. *Sorbic Acid* ($C_8H_4O_8$,$2HO=\overline{Ma}$).

The existence of a distinct acid in apple-juice was first proved by Scheele, in 1784: it was thence called Malic acid. In 1815 Donovan found it in the berries of the mountain-ash (*Sorbus aucuparia*). It occurs in other vegetables, especially (with oxalic acid) in the stalks of garden rhubarb. It is obtained from the clarified juice of ripe mountain ash-berries, by adding to it acetate of lead, washing the precipitate with cold water, then pouring boiling water upon the filter, and allowing it to pass through the precipitate into glass jars: after some hours, crystals of malate of lead are deposited, which are to be boiled with 2·3 times their weight of dilute sulphuric acid, sp. gr. 1·09; the clear liquor then poured off, and while still hot, sulphuretted hydrogen passed through it to precipitate the remaining lead; the liquid, after having been boiled and filtered, is a solution of nearly pure malic acid. It crystallizes with difficulty in deliquescent prisms. The *malates* are either acid or neutral, the acid being bibasic. They are mostly soluble in water, and insoluble in alcohol. Lime-water is not rendered turbid by malic acid, but on evaporating the solution, crystalline malate of lime separates, which is redissolved by boiling. These characters distinguish malic acid from oxalic, tartaric, racemic, and citric acid. The peculiar and brilliant crystalline appearance which recently precipitated malate of lead assumes when left in the liquid, is characteristic of this salt. A mixture of malate of lime and water, with a little yeast, gradually ferments; carbonic acid is given off, and succinic and acetic acids are found in the residue.

$$\overbrace{3(C_8H_4O_8,2HO)}^{\text{Malic acid.}} = \overbrace{2(C_8H_3O_5,3HO)}^{\text{Succinic acid.}} + \overbrace{(C_4H_3O_3,HO)}^{\text{Acetic acid.}} + 4CO_2 + 2HO.$$

Action of Heat on Malic Acid.—When this acid is heated up to about 400°, it is resolved into water and a crystalline sublimate of *Maleic Acid* (p. 634); but if the heat is carefully maintained between 270° and 280°, the product is *Fumaric* or *Paramaleic Acid*, an acid found in Fumitory, and isomeric with maleic acid: it is especially characterized by the insolubility of the fumarate of silver: according to Dessaignes, a liquid containing one-200,000th of fumaric acid, gives a precipitate with nitrate of silver.

TANNIC ACID; TANNIN; QUERCITANNIC ACID; GALLOTANNIC ACID ($C_{54}H_{22}O_{34}$,$=\overline{Qt}$).

There are many vegetable substances containing a principle which confers upon them an *astringent taste*, and which has the property of forming a precipitate in a solution of gelatine, and of striking a dark-blue or black precipitate with solutions of the persalts of iron. These properties are possessed in a remarkable degree by an infusion of *gall-nuts*—the excrescences which form upon the branches and shoots of the *Quercus infectoria*, being produced by the puncture of the female of the *Cynips gallæ tinctoriæ*. The insect deposits its ovum in the puncture, and occasions the excrescence, or gall, within which the larva is developed, and when the insect is perfect, it eats its way out. The best galls, known as *black* or *blue balls*, are gathered before the insect has escaped; the *white galls* are those from which the insect has departed, and are consequently perforated with a small circular hole. To obtain tannic acid, powdered galls are digested in about an equal weight of washed ether, containing about 10 per cent. of water, which, when poured off, separates into two portions, the heavier of which, when carefully evaporated, leaves tannic acid. It is an uncrystallizable scaly substance, of a pale buff color, very astringent, and soluble in water, alcohol, and ether: it reddens litmus, and remains unchanged when dry, but when moist it soon absorbs oxygen, and passes into gallic acid. Some of the acids and several salts precipitate its aqueous solution; and when boiled with dilute hydrochloric or sulphuric acid, it is converted into gallic acid and sugar.

$$C_{54}H_{22}O_{34} + 20HO = 3(C_{14}H_6O_{10}) + C_{12}H_{14}O_{14}$$

Tannic acid forms insoluble compounds with the greater number of bases, as well as with many organic substances, and especially the vegetable alkaloids. Combined with gelatin it forms leather, and in combination with peroxide of iron it is the basis of black dyes and *writing-ink*. No immediate precipitate is occasioned by tannic acid in very dilute solutions of pure protosalts of iron: but when the solutions are concentrated, a white gelatinous precipitate falls. If excess of tannic acid is added to a solution of persulphate of iron, a black precipitate is formed; and a similar precipitate falls in a solution of the protosulphate after due exposure to air.

The following, according to Dr. Miller, furnishes a good writing-ink: Digest three-quarters of a pound of bruised galls in a gallon of cold water, then add six ounces of sulphate of iron with an equal weight of gum arabic, and a few drops of creasote. Let this mixture digest at ordinary temperatures for two or three weeks, with occasional agitation, then let it settle, and decant for use. The tannoferric inks are liable to fade with age; but the writing may generally be restored by washing it with a weak acid, and then applying an infusion of galls, logwood, or ferrocyanide of potassium.

Characters of Tannic Acid.—1. When heated in air it melts, and burns like a resin. 2. It is precipitated by a solution of gelatin or albumen. 3. It gives a black precipitate or color in a solution of a neutral persalt of iron. 4. An excess of lime-water gives with it a dirty blue precipitate which rapidly becomes greenish colored. 5. The acid has a peculiarly astringent taste. It may be detected in all vegetable infusions or decoctions by their acquiring a dark color on the addition of a few drops of a persalt of iron.

Gallic Acid ($C_{14}H_6O_{10}$).

This acid was discovered in 1786 by Scheele: it was one of the results of the decomposition of tannic acid. It may be obtained by mixing powdered galls into a thin paste with water, and exposing it some weeks to air, occasionally adding water to prevent desiccation; the powder swells, becomes mouldy, and evolves carbonic acid, in consequence of a species of fermentation, during which gallic acid is formed. The magma is then pressed, the residue boiled in water, and the solution filtered while hot: on cooling, it deposits crystals of the acid, which may be purified by redissolving and boiling them with a little animal charcoal, when the filtered solution deposits white silky crystals of gallic acid. This acid is soluble in 100 parts of cold and in 3 of boiling water; readily soluble in alcohol, and sparingly so in ether. According to Strecker, it is a tribasic acid, represented in its anhydrous state by $C_{14}H_3O_7$, and forming 3 classes of salts, represented by $MO,2(HO),C_{14}H_3O_7,2(MO),HO,C_{14}H_3O_7$, and $3(MO),C_{14}H_3O_7$. When 1 part of gallic acid is triturated with 5 of sulphuric acid, gently heated, and dropped into water, a red crystalline substance falls (*Rufigallic acid*, $=2(HO),C_{14}H_4O_8$), which produces on mordanted calico a dye resembling madder-red.

Characters of Gallic Acid.—1. It is white and crystalline, soluble in water and alcohol. When heated in air it melts, and burns like a resin. 2. It produces an inky blue color with a persalt of iron. 3. It is not precipitated by nitrate of silver until boiled, when the silver salt is reduced. 4. It gives no precipitate with a solution of gelatin or albumen. 5. With an excess of lime-water it gives a white precipitate, which in air rapidly passes through shades of a blue and purple color. 6. When ammonia is poured on the crystals, they acquire a rich red color. 7. When the crystals are heated with a small quantity of sulphuric acid, they produce a rich crimson compound.

PYROGALLIC ACID ($C_{12}H_6O_6$) is now largely manufactured for the purposes of photography. It is obtained by sublimation from gallic acid, which, at a temperature between 410° and 420° is resolved into pyrogallic and carbonic acid (p. 497.) At a high temperature this acid is converted into water and a brown amorphous product, insoluble in water, but soluble in the alkalies, called *metagallic acid* (p. 498).

Pyrogallic acid forms white acicular and lamellar crystals, feebly acid, of an astringent bitter taste. The crystals melt at 257°, and sublime at about 400°. The acid is very soluble in water, alcohol, and ether. It is permanent when dry, but in aqueous solution soon becomes brown, as a result of oxidation, and under the influence of a free alkali, it rapidly absorbs oxygen (p. 141). It does not precipitate the pure protosalts of iron, but tinges them of a characteristic blue; it reduces most of the salts of mercury, silver, gold, and platinum. Dropped into milk of lime it produces a purple tint, which soon becomes brown. It is an important photographic agent (p. 475).

Characters of Pyrogallic Acid.—These have been described at p. 475. Its most characteristic property is the instant reduction of silver to the metallic state, from a solution of the nitrate. It differs from gallic acid in many respects. When the crystals are heated with a small quantity of sulphuric acid, a black compound results from some decomposition of the acid.

ELLAGIC ACID ($C_{14}H_2O_7 3HO$) is produced, together with gallic acid, during the exposure of moistened galls to air: it is a gray crystalline powder, insoluble in water but soluble in the alkalies, with which it forms sparingly soluble salts. This acid has been found in the intestinal concretions called *Oriental Bezoars.*

OXALIC ACID (C_2O_3HO).

This acid was discovered by Scheele in 1776: it is found in some fruits, in the juice of wood-sorrel and of common sorrel (*Oxalis acetosella; Rumex acetosa*), in the varieties of rhubarb, especially the *Rheum rhaponticum*, or pie-plant, and in several other plants: in these it is generally combined with potassa or lime. Certain lichens growing upon calcareous rocks, contain half their weight of oxalate of lime. It occasionally occurs in urine, as oxalate of lime. The mineral called *Humboldtite* is a peroxalate of iron. The commercial demands for oxalic acid are supplied from artificial sources. When 1 part of sugar is mixed with 4 of nitric acid and 2 of water, nitric oxide and carbonic acid are evolved; after distilling off the excess of nitric acid, and pouring the residue into a shallow vessel, crystals of oxalic acid are deposited, and on further evaporation of the mother-liquor, a second crop is obtained. The product is purified by solution in water and recrystallization. According to L. Thompson (*Pharm. Journ.*, viii. 117), one atom of sugar $=C_{12}H_{11}O_{11}$, and 7 atoms of nitric acid $=7NO_5$, are thus resolved into $7NO_2$, $6CO_2,2HO$, and $8(C_2O_3 3HO)$. These proportions, he observes, do not greatly differ from those employed by the wholesale makers, who use 112℔s of sugar, 560℔s of nitrate of potassa, and 280℔s of oil of vitriol, to produce 135℔s of crystallized oxalic acid, and 490℔s of sulphate of potassa.

Oxalic acid is now, however, chiefly manufactured from sawdust. It is thus produced of good quality, in large quantity, and at a much cheaper rate than in the process by the action of nitric acid on sugar. It has been long known that when woody fibre was heated to a moderate temperature with caustic potassa, the products were ulmic acid and hydrogen. At a higher degree of heat, oxalic acid replaces the ulmic as a product, and at a still higher degree, in which destructive distillation takes place, carbonic acid and hydrogen result. The principle of this new manufacture, therefore, is to heat the woody fibre with alkali, to a degree sufficient to produce oxalic, and neither ulmic nor carbonic acid. The sawdust is mixed with a solution of two equivalents of hydrate of soda and one of hydrate of potassa, having a sp. gr. of 1·25. Soda alone is not found to answer the purpose. The sawdust acquires a dark brown color from the action of the alkalies, and is rendered soluble in water. The mixture is heated to about 400° in shallow cast-iron pans for some hours, care being taken to avoid charring. The heat is then cautiously raised, and the result is a residue, containing a large quantity of the mixed oxalates of potassa and soda. A solution of carbonate of soda passed through the mixed oxalates on a filter, transforms the oxalate of potassa to oxalate of soda, the carbonate of potassa passing through the filter. The oxalate of soda is converted by lime to oxalate of lime, and this compound is decomposed by an equivalent of sulphuric acid. Oxalic acid remains in the liquid, and after two or three crystallizations is obtained in a pure state in large crystals. Two pounds of sawdust thus yield one pound of oxalic acid. Messrs. Dale and Roberts, of Manchester, who have perfected this process, manufacture nine tons of oxalic acid weekly for the purposes of calico-printing, dyeing, and bleaching.

The ordinary crystals of oxalic acid ($C_2O_3,HO+2HO$) are transparent four-sided prisms. They are intensely sour, and dissolve in about 12 parts of water at 60°, their solubility increasing rapidly with the increase of temperature; at 212° they fuse in their water of crystallization. They are less soluble in alcohol than in water, and still less soluble in ether: at a temperature of 100°, they gradually fall into powder, and lose about a third of their weight: after having been deprived of 2 equivalents of water, they sublime, when heated to about 320°; and the sublimate contains 1 atom of water. When the ordinary crystals are rapidly heated to about 350°, water, carbonic acid, carbonic oxide, and formic acid, are the results. Unlike other vegetable acids, oxalic acid is a powerful poison. A dose of it has destroyed life in ten minutes.

Hydrochloric acid dissolves oxalic acid without decomposition. It is not decomposed by dilute nitric acid, but when heated with concentrated nitric acid, it is converted into carbonic acid. Mixed with about 2 parts of sulphuric acid, and gently heated, it is rapidly resolved into equal volumes of carbonic acid and carbonic oxide, whilst the water of the crystals remains combined with the sulphuric acid (p. 244). The intensity of the acidity of oxalic acid is such, that 1 part in 200,000 of water reddens litmus. It abstracts lime from sulphuric acid when added to a solution of sulphate of lime, but oxalate of lead is decomposed by sulphuric acid; so that its affinity for bases appears to be about equal to that of sulphuric acid. When a solution of oxalic acid is boiled with the peroxides of manganese, lead, cobalt, or nickel, or with chromic acid, these oxides are partially reduced, carbonic acid is evolved, and oxalates are formed. When it is boiled with chloride of gold it throws down metallic gold, and carbonic acid passes off. Oxalic acid ranks among the most active irritant poisons, and the resemblance of its crystals to those of Epsom salt, has given rise to many fatal accidents. The antidotes are chalk or magnesia.

OXALATES.—In the neutral oxalates the oxygen of the base is to that of the acid as 1 : 3, their formula being MO,C_2O_3; and if the oxygen of the base be added to the acid, the result is a metal and carbonic acid, or $M,2[CO_2]$. Some oxalates, when heated, give this result: thus oxalate of silver yields, when heated, metallic silver and carbonic acid; $AgO,C_2O_3=Ag+2[CO_2]$. Sometimes carbonic oxide and carbonic acid are given off, leaving a protoxide of the metal; this is the case with oxalate of manganese; $MnO,C_2O_3=MnO,+CO,+CO_2$; and sometimes the carbonic oxide thus evolved reacts on the metallic oxide, and reduces it; thus with oxalate of cobalt, $CoO,C_2O_3=CoO+CO+CO_2$; and $CoO,+CO=Co+CO_2$. When the oxalates are heated with sulphuric acid, they are decomposed, and yield carbonic oxide and carbonic acid. In the acid oxalates, the quantity of acid is either twice, or four times, that contained in the neutral oxalates.

Oxalate of Ammonia ($NH_4O,C_2O_3,+HO$) is obtained by saturating a hot solution of oxalic acid by carbonate of ammonia, and crystallizing. It forms prismatic crystals, soluble in 28 parts of cold water. They are insoluble in alcohol. Added to any soluble compound of lime, this salt produces an insoluble *oxalate of lime*, provided no excess of acid be present; hence its use as a test of the presence of lime. The crystals contain two atoms of water. There is a binoxalate as well as a quadroxalate, but these are unimportant salts.

Oxamide ($C_2O_2NH_2$).—When oxalate of ammonia is subjected to dry distillation, it fuses, boils, decomposes, and volatilizes, leaving a little carbon behind; the liquid which passes over contains a flocculent substance, which also lines the neck of the retort, and to which Dumas gave the name of *oxamide;* it may be separated by washing and filtration, 100 parts of the oxalate yielding about 5. The other products of the decomposition are ammonia, water, carbonic acid, carbonic oxide, and cyanogen. Oxamide is also formed by the action of ammonia on oxalic ether; and of boiling nitric acid upon ferrocyanide of potassium. Oxamide forms a granulated powder, without taste or smell, and having no action on test-papers. It is volatile when carefully heated: it is scarcely soluble in water at 60°, and a saturated solution at 212° deposits it in flocculi. It is insoluble in alcohol. Boiled with potassa, or soda, oxamide evolves ammonia, and the carbon and oxygen remain in the state of oxalic acid. Dilute sulphuric, nitric, and hydrochloric acids convert it into oxalic acid, and form ammoniacal salts. Boiled with concentrated sulphuric acid, oxamide affords sulphate of ammonia, and equal volumes of carbonic acid and carbonic oxide are disengaged: concentrated nitric acid converts oxamide into nitrate of ammonia and carbonic acid.

Referring to the ultimate elements of oxamide, Dumas regards it is an amide of carbonic oxide, or as containing the hypothetical radical amidogen, NH_2 (p. 168).

Oxamic Acid ($C_4H_3O_6N$).—This compound is one of the results of the careful destructive distillation of binoxalate of ammonia, which at a temperature of about 450° leaves a residue of oxamide and oxamic acid; the latter is soluble in water, and when added to a soluble lime or baryta salt, it gives a crystalline precipitate, which is an oxamate of the base, and may be decomposed by sulphuric acid. Oxamic acid is a yellowish powder, which when boiled in water is reconverted into binoxalate of ammonia, $C_4H_3O_6N+2HO,=NH_4O,C_4O_6,HO$.

Oxalates of Potassa.—There are three of these oxalates: the neutral salt is with difficulty crystallizable. The *binoxalate* forms rhombic prisms, including 3 atoms of water, one of which is basic: it has a very sour taste, and is prepared in some parts of Germany and Switzerland from the juice of the wood-sorrel: it is often used for the removal of ink-stains and iron-moulds from linen. The *quadroxalate* is formed by the action of hydrochloric acid on the binoxalate, which abstracts half the potassa: it crystallizes in octahedra.

Oxalate of lime exists in many plants, and is found in such quantities in some lichens (especially *Variolaria communis*, *Isidium corallinum*, *Psora candida*, &c.), that the soil upon the spots on which they have grown and decayed, and trunks of trees upon which they have flourished, abound in it. The bodies called *raphides*, found in the cellular tissue, and floating occasionally in the juices of vegetables, are composed of oxalate of lime; this salt also exists occasionally in the human urine, and forms calculi, which, from their nodular exterior and reddish-brown color, are called *Mulberry calculi*. On adding oxalate of ammonia to any solution of lime, oxalate of lime is precipitated: it is insoluble in water, in excess of oxalic acid, and in acetic acid, but dissolves in hydrochloric and nitric acids: hence, in testing acid solutions for lime by oxalate of ammonia, an excess of acid should be previously neutralized. It is decomposed by sulphuric acid. When oxalate of lime is digested in a solution of a carbonated alkali, carbonate of lime and an alkaline oxalate are formed. When rendered dry upon a sand-heat, this salt becomes singularly electrical on friction, and platinum and other metals rubbed against the powder become negative, the powder positive; it appears to stand at the head of the substances which become positive by friction. (FARADAY.) At a red heat it is converted first into carbonate and then into quicklime. When well washed, and dried at 212° till it ceases to lose weight, it is CaO,HO,C_2O_3, and contains 38·4 per cent. of lime.

Of the other oxalates those of lithia, strontia, and alumina, are soluble in water; those of baryta, lead, and silver, are nearly insoluble in water, but are dissolved by a solution of sal-ammoniac. The double oxalate of potassa and chromium forms crystals of an intense blue color.

Characters of Oxalic Acid.—Tests as a *poison*: 1. This acid crystallizes in well-defined quadrilateral prisms. 2. When the crystals are heated on platinum, they melt, and are volatilized without combustion, and without leaving any carbonaceous residue. 3. Lime-water, or a solution of sulphate of lime, produces a white precipitate, not soluble in any vegetable acid, but it is dissolved by nitric acid. 4. A solution of the acid gives a white precipitate with nitrate of silver (oxalate of silver). This may be boiled without undergoing decomposition. When collected in a filter, washed, dried, and heated, it is decomposed, with slight detonation, into carbonic acid and metallic silver, $AgO+C_2O_3=Ag+2CO_2$. The crystalline form and volatility, the action of sulphate of lime and nitrate of silver, are the most reliable tests in cases of poisoning. By reason of its solubility in alcohol, oxalic acid may be separated from many organic substances. The aqueous solution of the acid, acidulated with acetic acid, should be precipitated by a solution of acetate of lead: the oxalate of lead collected, and this compound decomposed by a current of sulphuretted hydrogen. By this process, oxalic acid may be obtained in a crystalline state on evaporating the aqueous filtrate.

ACETIC ACID ($C_4H_4O_4$, or $C_4H_3O_3,HO$).

There are two principal sources of acetic acid, namely, 1. Vinous fermentation, and 2. The destructive distillation of wood. Comparing the ultimate composition of alcohol with that of acetic acid, it appears that 1 equivalent of alcohol, by the absorption of 4 equivalents of oxygen, is resolvable into 1 equivalent of acetic acid and 2 of water.

$$\underbrace{C_4H_6O_2}_{\text{Alcohol.}} + O_4 = \underbrace{C_4H_4O_4}_{\text{Acetic acid.}} + 2HO.$$

This is the theory of the formation of vinegar by the action of air on wine, beer, and similar fermented liquors; but alcohol itself, or a mixture of alcohol and water, does not undergo this change unless some azotized organic matter is at the same time present.

Vinegar (from *vin aigre*) or the dilute acetic acid chiefly used for domestic purposes, varies in quality according to the sources whence it is obtained. The best French vinegar is made by putting wine into a cask already containing a little vinegar, and to which air has due access, the temperature of the factory being maintained at about 80°. In this country, beer, or a wort prepared for the purpose, is used as a source of vinegar. A good extemporaneous vinegar may be prepared by dissolving 1 part of sugar in 6 of water, with 1 part of brandy, and a little yeast: this mixture is put into a cask, with the bunghole open, and kept at a temperature of between 70° and 80°: in from four to six weeks, the clear vinegar may be drawn off. Liebig recommends 120 parts of water, 12 of brandy, 4 of brown sugar, 1 of tartar, and ½ of sour dough, left for some weeks in a warm place, as ingredients for the production of a good vinegar. Various modes of accelerating acetification have been suggested by the extension of the surface of the liquid. As far back as 1743, Boerhaave recommended that a mixture of 1 part of alcohol and 9 of water should be made to trickle slowly through beech-shavings, previously soaked in vinegar, and lying loosely in a cask perforated with holes: the best proportions are, 1 part of alcohol (sp. gr. 0·848) with 4 to 6 of water, and a thousandth part of ferment, honey, or extract of malt. This mixture, previously heated to about 80°, is made to trickle through the shavings steeped in vinegar; the temperature, as a result of the oxidation of the liquid, soon rises to 100° or 104°, and remains stationary if all goes on favorably. When the liquid has been passed through the shavings three or four times, it is completely acetified: this may occupy from 20 to 36 hours. If the supply of air is deficient, part of the alcohol remains in the state of aldehyde, which escapes, and occasions a loss of acetic acid. The presence of essential oils, or of pyroligneous acid, prevents the acetification.

Vinegar is apt to be infested by *flies* (*Musca cellarus*), and by animalcules, commonly termed *eels* (*Vibriones aceti*); these may be destroyed by passing the vinegar through a spiral tube immersed in boiling water, or by heating it in a hot-water bath. When vinegar is exposed to air, it gradually becomes turbid, or mothery, losing its acidity, and depositing a gelatinous *conferva*, the vinegar-plant, which, by reason of holding vinegar like a sponge, causes acetous fermentation in saccharine liquids. The vinegar becomes weak and mouldy as these changes go on, and they are rapid in proportion to its weakness.

The adulteration of vinegar by sulphuric or by hydrochloric acid may be detected by nitrate of baryta and nitrate of silver, the precipitates being insoluble in nitric acid; but traces of sulphuric acid are found in all vinegars (from sulphates in the water), and their presence must be allowed for in using the barytic test. If nitric acid is present in vinegar, it destroys the color of an acid solution of sulphate of indigo, when boiled with it. In order, as it is said, to prevent vinegar becoming mouldy, it is allowed by law to contain one-thousandth part of its weight of sulphuric acid.

The specific gravity of vinegar depends more upon the foreign matters which it contains, than upon its actual strength, so that its value cannot be judged of by that criterion: the density of the best vinegar is about 1·020 to 1·025. To ascertain the proportion of *real acetic acid* which it contains, it must be cautiously neutralized by carbonate of soda, the quantity of this salt requisite for the purpose, indicating the proportion of real acetic acid present, 53 parts of *dry* carbonate of soda being equivalent to 51 of anhydrous acetic acid. The equivalent of carbonate of lime, which is 50, is so near that of acetic acid, as to furnish a ready mode of ascertaining the value of vinegar or other dilute acetic acid. For this purpose a piece of clean white marble is selected and accurately weighed; it is then suspended by a thread in a proper quantity of the vinegar to be examined, which is occasionally cautiously stirred, so as to mix its parts without chipping the marble; this, when it is no longer acted on, is removed, washed, dried, and weighed; its loss is equivalent to the acetic acid. Another mode of ascertaining the strength of vinegar consists in neutralizing it by hydrate of lime; acetate of lime is extremely soluble, so that the quantity of acetate of lime formed and dissolved, is directly as the quantity of acid present, and the *density* of the resulting solution of acetate of lime is in the same ratio. (*See* J. and P. TAYLOR on an *Acetometer*, *Quart. Journ.*, vi.) "An ounce of good vinegar should saturate about 30 to 32 grains of pure and dry carbonate of potassa: such vinegar contains about 5 *per cent.* of *anhydrous acetic acid*, and its density is from 1·01 to 1·03." (LIEBIG.)

Distilled Vinegar.—When vinegar is carefully distilled, the first portion which passes over usually contains a little alcohol; this is followed by dilute acetic acid, which, towards the end of the process, often acquires an empyreumatic odor; the residue is brown, acid, and has a burned flavor. According to R. Phillips (on the *London Pharmacopœia*), when the best English malt-vinegar, of the specific gravity of 1·024 is distilled, the first eighth part which passes over is of the specific gravity 0·99712, so that it contains a little alcohol; a fluid ounce of it, = 1·8047 cubic inches, dissolves from 4·5 to 5 grains of precipitated carbonate of lime: the next six-eighths have the specific gravity 1·0023, and a fluid ounce dissolves 8·12 grains of the carbonate; a fluid ounce of the acid, of specific gravity 1·007, dissolves 15 to 16 grains of precipitated carbonate of lime, or 13·8 grains of marble.

Distilled vinegar is colorless, and it has not the agreeable flavor and odor of the original vinegar; it contains a trace of alcohol and of acetic ether, and also a peculiar organic matter. When distilled from a copper-still through a pewter worm, it becomes discolored by sulphuretted hydrogen from the presence of traces of copper, lead, or tin, so that silver or earthen condensers are used by the wholesale distillers.

PYROLIGNEOUS ACID.—The production of vinegar by the destructive distillation of wood, was one of the numerous discoveries of Glauber; and a large quantity of acetic acids, of all strengths, is now derived from this source. The wood is heated in iron retorts, connected with a proper condensing apparatus, and the inflammable gaseous products are conducted into the furnace, so as to serve as fuel. The hard woods, such as beech, oak, birch, and ash, are selected, and previously dried. The liquid products are water, wood-spirit, or naphtha, tar, and acetic acid (p. 565): these are drawn off from the floating tar, and distilled, when the wood-spirit first passes over, and afterwards the acetic acid, still, however, very impure from the presence of tar and other matters. This impure acid is then saturated either by soda or by chalk, and the *acetate* so formed is carefully heated, so as to decompose or expel the tarry matters without decomposing the salt, which is then further purified by solution and crystallization, and ultimately decomposed by distillation with sulphuric acid diluted with about half its weight of water. The acetic acid which passes over is purified by redistillation. The sulphate of soda resulting from this process may be used to convert the crude acetate of lime to acetate of soda and sulphate of lime, when chalk has been used for the saturation of the crude acid.

The purest acetic acid, obtained by the decomposition of an acetate by sulphuric acid, contains an atom of water ($HO,\overline{Ac}$), which, in the formation of the neutral acetates, is replaced by an atom of base.

For our knowledge of the *anhydrous* acid ($C_4H_3O_3$), we are indebted to Gerhardt. It may be obtained by distilling 8 parts of dry acetate of potassa with 3 of oxychloride of phosphorus; the distillate is returned upon the residue and redistilled, and the product again rectified.

Anhydrous acetic acid, sometimes represented as the teroxide of the compound radical *acetyle* (C_4H_3), is a colorless liquid, of a peculiar odor; (sp. gr. 1·07); its boiling-point is 280°, and the sp. gr. of its vapor is 3·47. When dropped into water, it falls to the bottom like heavy oil, but soon dissolves on agitation; it readily absorbs moisture when exposed to air. Acted upon by potassium it evolves hydrogen, and forms acetate of potassa, and an oily product of an agreeable odor. It dissolves chloride of phosphorus, producing phosphorous acid and oxychloride of acetyle.

Monohydrated Acetic Acid or Glacial acetic acid ($C_4H_3O_3HO$).—This is obtained by distilling 1 equivalent of fused acetate of soda with 2 equivalents of sulphuric acid, and placing the distillate in ice; the congealed product is then suffered to drain, by inverting the bottle, and in that frozen state, it is the pure monohydrated acid. Its crystals are plates or tufts, which fuse at about 50°. It has a strong pungent odor, agreeable when diluted, and is powerfully acid and caustic, reddening and blistering the skin. It boils at 243°, and its vapor is inflammable: it absorbs moisture from the air, and dissolves in all proportions in water. The sp. gr. of the liquefied crystallized acid is 1·0635 at 62°, and this density increases on dilution, until the acid contains 1 equivalent of anhydrous acid to 3 of water, when it is 1·073; on further dilution, its density diminishes, and when it consists of about equal weights of the acid and water, its sp. gr. is 1·063, or the same as that of the undiluted acid.

The monohydrated acid does not attack carbonate of lime until it is diluted; and when mixed with alcohol, it neither reddens litmus nor decomposes many of the carbonates (p. 543.) It is partially decomposed by passing it through a red-hot porcelain tube, yielding acetone, carbonic acid, and water.

$$2(C_4H_4O_4) \quad = \quad C_6H_6O_2 \quad + \quad 2CO_2 \quad + \quad 2HO$$

Its entire decomposition is only effected at a very high temperature; but when its vapor is passed over heated platinum-black, it is resolved into equal volumes of carbonic acid and light carburetted hydrogen ($C_4H_4O_4 = 2CO_2 + 2CH_2$).

Action of Chlorine on Acetic Acid.—When chlorine is passed through a mixture of 2 parts of glacial acetic acid and 1 of water (taking care to exclude the direct rays of the sun), it is slowly absorbed, and a compound is formed which has been termed *chloracetic acid*, $=HO,C_4H_2O_3Cl$: it is stated to produce definite salts, in which, when dilute, nitrate of silver gives no precipitate. This *chloracetate of silver* forms shining scales, soluble in water, and decomposed by light.

When glacial acetic acid is exposed to the action of gaseous chlorine, under the influence of the sun's rays, white deliquescent flocculi are formed $=HO,C_4Cl_3O_3$. This compound has been termed *trichloracetic acid;* in it the hydrogen of the anhydrous acetic acid is replaced by chlorine, but the reaction is more complex, inasmuch as chlorocarbonic, carbonic, and oxalic acids, are at the same time formed. This acid forms salts which are soluble in water, and which, when heated, evolve chlorocarbonic acid and carbonic oxide, and leave a chloride.

$$MO,C_4Cl_3O_3 \quad = \quad MCl \quad + \quad 2(CO,Cl) \quad + \quad 2CO$$

Sulphacetic Acid.—When acetic acid is acted on by anhydrous sulphuric acid, it loses 2 atoms of water, and a new acid $=C_4H_2O_2,2SO_3,2HO$, results: it forms deliquescent crystals, and bibasic salts.

ACETATES.—These salts are very numerous, and many of them of much importance in the arts. The neutral acetates, $=MO,C_4H_3O_3$, are all soluble in water; acted on by sulphuric acid they evolve acetic acid, recognized by its odor. They are mostly reddened by perchloride of iron. They are decomposed by a red heat, some of them giving off the acid and leaving the metal, such as the acetates of copper and of silver; some give off acetone and leave a carbonate, and some, which require a higher temperature for decomposition, afford acetone and other more complex products.

Acetate of Ammonia, obtained by neutralizing distilled vinegar by ammonia, has long been used in medicine, under the name of *Spirit of Mindererus.* When boiled, ammonia passes off and a *binacetate* is formed. These salts are very soluble in water and in alcohol, and are crystallized with difficulty.—*Acetate of Potassa* is very deliquescent; soluble in its weight of water at 60°, and in twice its weight of alcohol. When carefully fused, it concretes into a lamellar mass on cooling, the *terra foliata tartari,* or *febrifuge salt of Silvius,* of old pharmacy. It is present in the sap of many vegetables, and is a source of the carbonate of potassa found in their ashes. The aqueous solution of this acetate is not decomposed by carbonic acid; and a current of that gas passed through its alcoholic solution, precipitates carbonate of potassa, and sets free acetic acid (p. 50). Like the acetate of soda, it is decomposed when heated with caustic potassa or lime, and resolved into carbonate of potassa and Marsh gas (p. 246). *Acetate of soda* is largely manufactured as a source of acetic acid, by the action of sulphate of soda on acetate of lime $(NaO,SO_3,+CaO,\overline{Ac}=NaO,\overline{Ac},+CaO,SO_3)$, (p. 596). It crystallizes in rhombic prisms with 6 atoms of water. It bears a dull red heat without decomposition.—*Acetate of baryta* forms efflorescent crystals with 1 atom of water, if obtained at 80°, but 3 if at 32°. By heat this salt is resolved into carbonate of baryta and acetone, $2(BaO,C_4H_3O_3=(BaO,CO_2)+(C_6H_6O_2)$.—*Acetate of lime* forms silky prisms, soluble in water and in alcohol. When heated to about 230° and triturated, it is phosphorescent.—*Acetates of alumina,* prepared by decomposing solutions of sulphate of alumina or of alum by acetate of lead, are extensively used as mordants, by calico-printers. These acetates have been minutely examined by Mr. Crum (*Q. J. Chem. Soc.*, vii.)—*Protacetate of iron,* obtained by the action of acetic acid on the protosulphide, out of contact of air, forms white silky crystals. The *peracetate,* made by digesting iron turnings in the acid exposed to air, is a deep red solution, not crystallizable. It is used by dyers and calico-printers.—*Acetates of copper* constitute the varieties of *verdigris.* The common verdigris of commerce is a hydrated dibasic salt $=2(CuO),\overline{Ac}$, 3HO: it is prepared by exposing plates of copper to the action of acetic acid. The method now practised consists in alternating plates of copper with pieces of woollen cloth steeped in acetic acid; they gradually become covered with verdigris, which is removed in the form of a blue-green powder, and the operation repeated as long as the plate lasts. Sometimes husks and stalks of grapes or raisins, in a state of acetous fermentation, are employed to act upon the copper, as is the case with some of the French verdigris. This article is commonly packed in leather, and frequently adulterated with a mixture of chalk and sulphate of copper. Pure diacetate of copper forms small silky crystals of a greenish-blue color, which when heated at 212°, become green, and lose water: when moistened, this salt crumbles, and is only partially soluble in water, by which it is resolved into *tribasic* and *neutral* acetates. The *neutral acetate of copper* (*crystallized verdigris*) is made by dissolving common verdigris in acetic acid, and allowing it to crystallize upon twigs or pieces of string: it forms blue-green prisms, soluble in 5 parts of boiling water, and sparingly in alcohol. When its dilute solution is boiled, it deposits a tribasic salt: if boiled with sugar, a crystalline precipitate of suboxide of copper is formed.—*Acetates of lead.* When oxide of lead is dissolved in excess of acetic acid, prismatic crystals are obtained on evaporating the filtered solution $=PbO,C_4H_3O_3,3HO$. This salt, known as *sugar of lead*, generally occurs in the form of a crystalline mass, slightly efflorescent, soluble in less than two parts of water, and in about 8 parts of alcohol. When heated, it first becomes anhydrous, then fuses, and at a higher temperature is converted into a *subsesquiacetate* $=3(PbO),2(C_4H_3O_3)$, soluble in water and alcohol, and having an alkaline reaction. When 7 parts of litharge and 10 of sugar of lead are boiled together in 30 parts of water, a solution of a *tribasic acetate* $=(3(PbO),C_4H_3O_3)$ is formed, known in pharmacy as *Goulard's extract of lead;* this salt may be obtained in acicular crystals, having an alkaline reaction. Its decomposition by carbonic acid, is one of the processes for making white lead, has been elsewhere noticed (p. 402). This subacetate is a delicate test for the presence of carbonic acid, which it absorbs from the atmosphere, or from any liquid containing it: even distilled water is seldom so free from carbonic acid as not to be rendered turbid by the addition of a few drops of this salt, and with all spring and river water it forms a more or less turbid white mixture. When excess of minium is heated in glacial acetic acid to about 105°, the solution deposits prismatic crystals on cooling, composed of *peroxide and acetate of lead;* they are very unstable, and on attempting to dry them are decomposed into peroxide of lead and acetic acid. *Acetate of suboxide of mercury* ($Hg_2O,\overline{Ac},$) is formed by mixing solutions of acetate of potassa and nitrate of suboxide of mercury; it forms micaceous crystalline plates requiring 600 parts of cold water for solution. The acetate of the red oxide is readily soluble. *Acetate of silver* is deposited in lamellar crystals when acetic acid is added to a strong solution of nitrate of silver; and it is abundantly precipitated from the nitrate by acetate of soda. This, and the preceding, are the only difficultly soluble neutral acetates.—*Acetate of uranium* forms a series of double salts with basic acetates, which have been described by Wertheim. (*Ann. Ph. et Ch.*, 3ème sér. xi. 49.)

Characters of Acetic Acid and the Acetates.—1. Acetic acid at ordinary temperatures is liquid, and has a powerful and peculiar odor. 2. It is entirely volatile if pure, and the vapor of the concentrated acid is combustible, burning with a pale reddish flame. 3. It is not precipitated by lime-water, acetate of lead, or nitrate of baryta or silver, if free from sulphuric and hydrochloric acids.

An *acetate* may be identified by boiling it with sulphuric acid: the vapor of acetic acid is evolved. This may be recognized by its odor, volatility, and acid reaction. Acetic acid sometimes contains lead, silver, or copper, as an impurity. The first may be detected by sulphuretted hydrogen, producing a brown color: the second by the action of the gas, and the production of a white precipitate by hydrochloric acid: the third by the action of ammonia (p. 394). Acetate of soda may be present in the acid: this is detected by the yellow color imparted to flame.

ACETONE ($C_6H_6O_2$).—This product is obtained when acetate of lime is distilled with excess of quicklime, or when 2 parts of acetate of lead and 1 of lime, well mixed, are heated in an iron retort connected with a proper condensing apparatus. The distillate is rectified, and finally redistilled from a water-bath. Pure acetone is a colorless liquid of a peculiar aromatic odor and pungent taste. Its sp. gr. 0·792; it boils at 132°; the sp. gr. of its vapor is 2·022; it dissolves in all proportions in water, alcohol, and ether; but chloride of calcium and caustic potassa separate it from its aqueous solution. It is very inflammable and burns with a bright flame. By the action of chlorine upon acetone, three substitution-products are obtained, in which 2, 3, and 4 atoms of its hydrogen are replaced by chlorine.

FORMIC ACID (C_2H,O_3,HO)

was first noticed, in 1670, in the body of the *red ant* (*Formica rufa*) and was obtained by distilling the bruised insects with water. It may be artificially produced by many processes founded upon the oxidation of various organic products. Dobereiner procured it by the distillation of 10 parts of starch, 37 of peroxide of manganese, 30 of water, and 30 of sulphuric acid, until 30 parts had passed over: or by distilling a mixture of 10 parts tartaric acid, 3 of peroxide of manganese, 3 of sulphuric acid, and 3 of water. In these cases, capacious retorts must be used, to allow of the effervescence which ensues. The acid distillate, which is very dilute, is saturated with carbonate of lead, and the resulting formate of lead purified by crystallization during the cooling of its solution in boiling water; it is then decomposed, either by an equivalent of sulphuric acid, or by the action of sulphuretted hydrogen. Formic acid has also been obtained by distilling a mixture of oxalic acid, and glycerine, at a temperature of about 212°; in this case, the oxalic acid is resolved into formic and carbonic acids.

$$2(HO,C_2O_3) = (HO,C_2HO_3) + 2(CO_2).$$

The glycerine remains unchanged, provided the temperature does not exceed 220°. There is reason to believe that the poison of the wasp and bee, as well as that of the vesicles on the leaf of the stinging-nettle (*Urtica dioica*), is formic acid in a concentrated state.

Monohydrated formic acid is a very acrid fuming liquid, of the sp. gr. 1·22; crystallizable below 32°, boiling at about 220°, and yielding an inflammable vapor, the density of which is 2·125. The anhydrous acid has not been isolated. It is easily converted by oxidation into carbonic acid and water: when boiled, either with oxide of mercury or oxide of silver, this oxide is reduced, with the escape of carbonic acid, ($2AgO, + C_2H_2O_4, = 2Ag, + 2CO_2, + 2HO$). Chlorine converts it into carbonic and hydrochloric acids ($C_2H_2O_4, + 2Cl, = 2CO_2 + 2HCl$). Formic acid is frequently represented as the teroxide of the compound radical *formyle* ($C_2H + O_3$). Its elements are in the proportions to form 2 atoms of carbonic oxide and one of water, ($C_2HO_3 = 2CO + HO$).

Formates.—The neutral formates are=(MO,C_2HO_3). They are all soluble: when heated with excess of sulphuric acid, they yield carbonic oxide and water; and with caustic potassa they evolve hydrogen, and are changed into carbonates.—*Formate of ammonia*, when heated to about 400°, is resolved into hydrocyanic acid and water, $NH_4O,C_2HO_3 = (C_2N,H) + 4HO$.—*Formate of lead*, when heated to about 375°, evolves carbonic acid and hydrogen, and leaves metallic lead: it requires 40 parts of cold water for solution, but is very soluble in boiling water.—*Formate of copper* crystallizes in large blue prisms: it forms double salts with the formates of baryta and of strontia.

Characters of Formic Acid.—This acid may be identified by its odor, volatility, and its reducing power on the salts of silver and gold.

BENZOIC ACID ($C_{14}H_5O_3,HO$).

This substance is found ready formed in *benzoin*, the resinous exudation of the *Styrax benzoin*, a tree growing in Sumatra, Borneo, and Java. *Tolu* and *Peru Balsam* also contain it, in common with *Cinnamic acid;* and it is a product of the oxidation of *bitter-almond oil.* It is found in the pods of the Vanilla. It is generally obtained from benzoin, either by sublimation, or in the humid way, by the action of bases: the amount of the product is various, depending upon the quality of the benzoin, upon the process selected, and the care with which it is conducted; it fluctuates from 4 to 10 per cent. The process usually resorted to consists in coarsely pulverizing the benzoin, and heating it in a shallow vessel, over which a sheet of coarse blotting-paper is stretched, surmounted by a cone of thick paper, or by a wooden receiver, if the operation is carried on upon the large scale. The layer of benzoin should not be more than two or three inches in thickness, and the heat gradually and regularly applied, so as slowly to sublime the acid, the vapor of which, passing through the bibulous diaphragm, condenses in a crystalline form in the cone or recipient, empyreumatic oil at the same time evolved, is retained and absorbed by the paper. (MOHR.) Benzoic acid may also be obtained by triturating benzoin with half its weight of hydrate of lime, and adding 10 parts of water; after the mixture has digested for some hours, it is boiled and filtered: the filtrates are then concentrated, and saturated, whilst hot, by hydrochloric acid; on cooling, benzoic acid is deposited, which must be again dissolved and crystallized. (SCHEELE.)

Benzoic acid is inodorous; but, as it is obtained by sublimation, it has an agreeable odor, derived from a trace of volatile oil; it generally forms acicular crystals. It has a slightly sour and acrid taste. It melts at about 250°, and on cooling, congeals into a crystalline mass. At about 295° it sublimes: about 460° it boils, and forms an acrid vapor, the sp. gr. of which is 4·26. This acid requires 200 parts of water at 60°, and 30 parts at 212°, for its solution; the saturated boiling solution concretes on cooling into a crystalline mass. It dissolves in about twice it weight of alcohol, and is precipitated on dilution with water. It also dissolves in ether, and in fixed and volatile oils. In its usual crystalline form it contains an atom of water, its equivalent being 122; that of the anhydrous acid is 113.

It has been found convenient, in reference to the numerous compounds of the benzoic series, to regard them as derived from a compound radical, to which the term *Benzoyle* has been applied; and which has been obtained, in the form of an oil, by the dry distillation of benzoate of copper; its formula is $C_{14}H_5O_2,=Bz$. It is obvious that benzoic acid ($C_{14}H_5O_2+O$) may be regarded as an oxide, and bitter-almond oil ($C_{14}H_5O_2+H$) as a hydride of this radical, and that it may be assumed as the basis of the numerous derivatives of those bodies. But the term *Benzoyle*, or *Benzule*, is perhaps more appropriately confined to the fundamental hydrocarbon ($C_{14}H_5$) of the series.

Anhydrous benzoic acid has been obtained by the action of oxychloride of phosphorus on anhydrous benzoate of soda; it is insoluble in water, but soluble in boiling alcohol and in ether: by continuous boiling in water it reverts to the ordinary hydrate.

Benzoates.—These salts are represented by the general formula $MO,C_{14}H_5O_3$: they are mostly soluble in water and in alcohol. Benzoate of lime dissolves readily in boiling water. Basic benzoate of peroxide of iron is so little soluble in water that an alkaline benzoate has been used to precipitate iron, and to separate this metal from some other oxides.

Chlorobenzoic acid is the result of the action of the sun's rays on benzoic acid in dry chlorine. In it an atom of hydrogen is replaced by one of chlorine, giving $C_{14}H_4O_3,Cl$. There are also two other of these chlorine compounds, in which 2 or 3 atoms of hydrogen are displaced by a similar number of atoms of chlorine. A similar bromine compound has also been obtained.

Sulphobenzoic acid is the product of the action of anhydrous sulphuric on benzoic acid: it is dibasic, and is represented as $2(HO),C_{14}H_4S_2O_8$.

Nitrobenzoic acid ($HO,C_{14}H_4O_3,NO_4$) is a compound in which an atom of hydrogen is replaced by an atom of nitrous acid. The nitrobenzoates are mostly crystallizable and soluble in water and alcohol: when suddenly heated they deflagrate.

Benzamic acid. Carbanilic acid. Amidobenzoic acid.—This is one of the results of the action of sulphuretted hydrogen upon an alcoholic solution of nitrobenzoate of ammonia: it is represented as benzoic acid, in which an equivalent of hydrogen is replaced by an equivalent of amidogen ($C_{14}H_4(NH_2)O_3$).

HYDRIDE OF BENZOYLE. *Essential oil of bitter almonds* ($C_{14}H_5O_2+H$, or $C_{14}H_6O_2$).—Bitter almond oil is obtained by macerating the pulverized bitter-almond cake, after the fixed oil has been expressed, in water heated to about 100°, for 24 hours, and then distilling; it passes over with the vapor of water, and condenses in the form of a heavy oil, the supernatant water holding a portion of it in solution. This oil is combined with hydrocyanic acid, and is therefore, as well as the bitter almond water, very poisonous. It may be obtained also from peach and apricot kernels, from the leaves of the laural (*Prunus laurocerasus*), and from the bark of the wild cherry (*Prunus padus*). To free it from hydrocyanic acid, the oil may be agitated with milk of lime and a solution of protochloride of iron, and redistilled.

Pure bitter-almond oil is a colorless liquid of a peculiar and agreeable aromatic odor and a pungent flavor. It is not poisonous, and as it is much used in confectionery and cookery, care should be taken that for such purposes its purification has been adequately performed. Its boiling-point is about 350°. It is easily inflammable, and burns with a bright sooty flame. It is soluble in about 30 parts of water, and in all proportions in alcohol and ether. Its alcoholic solution constitutes the *Essence of bitter-almonds* commonly sold for culinary purposes; it usually consists of one part of the oil dissolved in 7 of alcohol. When this oil is exposed to air it absorbs oxygen and is converted into crystallized benzoic acid: $C_{14}H_6O_2+O_2,=C_{14}H_6O_4$.

Neither bitter-almond oil nor hydrocyanic acid exists ready formed, in the almond or sources whence they are obtained, but they are produced by the mutual agencies of certain azotized substances, under the influence of water and a due temperature; these substances are *amygdaline*, and *emulsin* or *synaptase.*

Amygdaline ($C_{40}H_{27}O_{22}N$) is found in bitter-almonds, in the leaves and berries of the cherry laurel, and the bitter kernels of the species of *amygdalus* and *prunus.* To obtain it, the pulverized cake of bitter-almonds which remains after the expression of the fixed oil, is boiled in repeated portions of alcohol of sp. gr. 0·820. These alcoholic liquids are then distilled in a water-bath, till the residue acquires a syrupy consistence, when it contains little else than amygdaline and sugar; to get rid of the latter, the liquor is diluted with water, and a little yeast having been added, it is placed in a warm situation, to ferment; when the fermentation has ceased, the liquor is filtered, and again evaporated to the consistence of syrup; excess of cold alcohol is then added, which throws down the amygdaline in the form of a white crystalline powder. From three to four per cent. is thus obtained from bitter-almonds. Amygdaline is readily soluble in water, and the crystals deposited from its saturated aqueous solution are transparent prisms, containing 10·57 per cent. of water (= 6 atoms). It is inodorous and slightly sweet and bitter. When acted on by fixed alkalies, it evolves ammonia and forms *amygdalic acid.*

$$\underbrace{C_{40}H_{27}O_{22}N}_{\text{Amygdaline.}} + KO,HO + HO = \underbrace{KO,C_{40}H_{26}O_{24}}_{\text{Amygdalate of potassa.}} + NH_3$$

The action of emulsine upon amygdaline in the production of bitter-almond oil, was first explained by Wöhler and Liebig. When a solution of 10 parts of amygdaline in 100 of water is mixed with a solution of 1 part of emulsine in 10 of water, the mixture becomes opalescent, acquires the odor of bitter almonds, and, when distilled, yields hydride of benzoyle and hydrocyanic acid; these changes ensue most rapidly at a temperature between 85° and 105°. Boiling water and boiling alcohol destroy the action.

When expressed bitter-almonds are moistened and triturated with water, the same reaction ensues; and if water enough be present to dissolve the oil as it is formed, the whole of their amygdaline disappears: to obtain the full proportion of oil, 1 part of bitter-almond cake should be macerated for 24 hours in 20 parts of water, at about 100°, and then subjected to distillation. Seventeen grains of amygdaline dissolved in an ounce of emulsion of sweet almonds, yield a solution containing 1 grain of anhydrous hydrocyanic acid.

In the fermentative changes which ensue during the mutual action of emulsine and amygdaline under the conditions above stated, bitter-almond oil and hydrocyanic acid are not the only products; sugar and formic acid are also formed. The general result may be represented as follows:—

$$\left.\begin{array}{l}\text{1 atom of amygdaline,}\\ C_{40}H_{27}O_{22}N\ .\ .\ .\end{array}\right\} = \left\{\begin{array}{lll} 1 & \text{atom of hydrocyanic acid .} & C_2H\quad N\\ 2 & \text{" hydride of benzoyle} & C_{28}H_{12}O_4\\ \frac{1}{2} & \text{" sugar . . . . .} & C_6H_6O_4\\ 2 & \text{" formic acid . . .} & C_4H_2O_6\\ 6 & \text{" water . . . . .} & H_6O_6\\ \hline & & C_{40}H_{27}O_{22}N\end{array}\right.$$

Action of Ammonia on Hydride of Benzoyle.—By agitating bitter-almond oil with ammonia and heating the mixture, a crystalline compound is formed, *hydrobenzamide* ($C_{14}H_{13}N_2$): it is changed by the action of potassa into an isomeric basic body, *benzoline* or *amarine,* the salts of which are intensely bitter. Some other azotized compounds are similarly produced.

When crude bitter-almond oil (retaining hydrocyanic acid) is digested with an alcoholic solution of caustic potassa, it is converted into a crystalline product, which has been termed *Benzoine,* represented as $=C_{28}H_{12}O_4$, and therefore isomeric with the hydride of benzoyle; but it is inodorous and tasteless. When its vapor is passed through a red-hot tube, it is resolved into bitter-almond oil. This curious product has been represented by the formula $C_{28}H_{11}O_4,H$, as the *hydride* of a radical, $=C_{28}H_{11}O_4$, called *stilbyl.* For further details in reference to these, and many other compounds derived from or connected with bitter-almond oil, we must refer to Laurent (*Ann. de Chim. et Ph.*, I. 291, 3ème sér.) and to Gerhardt (*Chim. Organ*).

HIPPURIC ACID ($C_{18}H_8O_5N,+HO$).

This acid is contained in the urine of herbivorous mammifera, and in small quantity in human urine, in which it may be produced by the use of benzoic acid: in passing through the system this is converted into hippuric acid. It may be obtained by adding milk of lime to fresh cow's urine, boiling, filtering, neutralizing the filtrate with hydrochloric acid, and evaporating it to about one-eighth of its bulk; excess of hydrochloric acid is then added, which throws down impure hippuric acid. It may be purified by dissolving it in boiling alcohol, which on cooling deposits it in colorless four-sided prisms with pointed terminations. It requires about 500 parts of water for its solution: it is abundantly soluble in boiling water and in alcohol, but less so in ether. It fuses when heated, and concretes into a crystalline mass on cooling. When long boiled with dilute nitric or hydrochloric acid, it yields benzoic acid and gelatine-sugar (glycocol or glycocine). Boiled with peroxide of lead, carbonic acid and benzamide ($C_{14}H_5O,NH_2$) are formed.—*Hippurates.* Those of the alkalies and earths are soluble and crystallizable; they give white precipitates in solutions of lead, mercury, and silver, and a brown precipitate with persalts of iron.

MECONIC ACID ($C_{14}HO_{11},3HO$).

The existence of a distinct acid in opium was announced by Seguin in 1804, and shortly afterwards by Sertuerner, who gave it the above name (from *μήκων, poppy*). It may be most conveniently extracted from the precipitate obtained by adding chloride of calcium to infusion of opium, in the process for procuring morphia. This precipitate is washed first in water, and then with hot alcohol, and mixed with ten times its weight of water, at 195°; hydrochloric acid is then gradually added, so as to dissolve the *meconate of lime* (which forms the bulk of the precipitate) and leave the sulphate of lime; the solution is filtered, and on cooling deposits crystals of *bimeconate of lime:* these are again dissolved in hot dilute hydrochloric acid, by which the lime is abstracted, and crystals of meconic acid obtained, which, if pure, should leave no residue when burned: they must be redissolved in the acid, and recrystallized, till they are obtained in this state, but care must be taken to keep the temperature of their solutions below 212°.

Meconic acid crystallizes in transparent and micaceous scales of an acid taste, soluble in 4 parts of hot water, and in alcohol. The crystals are permanent in the air, but when heated to 212° they lose 21·5 per cent. of water: they then sustain a temperature of 240° without decomposition; but if a strong aqueous solution of the acid is boiled, it becomes dark colored, carbonic acid is evolved, and oxalic acid and *comenic* (*metameconic*) acid are formed, together with a brown product. Boiled in hydrochloric acid, meconic acid is resolved into carbonic and comenic acid.

One of the principal characters of this acid and of its salts, is that of forming a compound with the peroxide of iron of an intensely red color, very similar to that of the sulphocyanide of iron, but differing in the fact that a solution of corrosive sublimate does not destroy the red color; hence a persalt of iron is an excellent test of its presence, and by it, opium may sometimes be recognized, when the quantity is so small as to render the morphia very difficult of detection. The red color is destroyed by heat, by sulphurous acid, and by protochloride of tin. Meconic acid in solution gives a yellowish-white precipitate with acetate of lead, and this precipitate is not dissolved by acetic acid.

CHAPTER LIII.

ALKALOIDS AND ORGANIC BASES. SUBSTANCES ASSOCIATED WITH OR DERIVED FROM THEM.

THESE are for the most part solid and crystallizable compounds. Some are volatile: others are fixed, and are readily decomposed when heated, or when brought in contact with chemical reagents. They generally contain an atom of *nitrogen* as one of their ultimate elements; they have a bitter taste, are sparingly soluble in water, more soluble in alcohol, but readily soluble in most of the dilute acids as well as in ether and chloroform. With tannic acid, and with excess of iodic acid, they generally produce precipitates. They are salifiable bases, and their compounds with the acids are decomposed and precipitated by the alkalies. The alkaloids are mostly crystallizable, and are represented by very high equivalent numbers. They restore the blue color to reddened litmus. They are found in plants united to certain acids, and usually forming neutral or acid salts, which, as well as their artificial combinations, are decomposed in the voltaic circle, and the base is evolved at the negative pole. Many hypotheses have been built upon the ultimate composition of these alkaloids, and some curious analogies pointed out respecting them by Liebig, Dumas, and others.

In consequence of the analogy that pervades these principles, one general method of separating them is applicable to all, though each may require peculiar modifications of it. The substance which contains them is boiled in water acidulated by hydrochloric acid, the decoction is filtered and neutralized by ammonia, lime, or magnesia, when the alkaloid is precipitated, and afterwards separated and purified by alcohol or ether. Much of the history of these bodies is connected with Materia Medica. We shall here examine them simply in reference to their chemical properties.

MORPHIA ($C_{35}H_{20}O_6N+2HO=\overset{+}{M}+2HO$).

In order to procure this alkaloid, a filtered solution of opium in tepid water is mixed with acetate of lead in excess; the precipitated meconate of lead is separated by a filter, and through the solution, containing acetate of morphia, now freed to a considerable extent from color, a stream of sulphuretted hydrogen is passed. The filtered, and nearly colorless liquid, from which the lead has been removed, may be warmed to expel the excess of gas, once more filtered, and then mixed with a slight excess of caustic ammonia, which throws down the morphia and narcotine; these may be separated by boiling ether, in which the latter is soluble. The meconate of lead, well washed, suspended in water, and decomposed by sulphuretted hydrogen, yields solution of meconic acid. The quantity of morphia obtained from opium is variable; the produce is greatest from Turkey opium, and least from the East Indian and Egyptian. The average is generally estimated at about 1 oz. from the pound. Good opium is considered to contain ten per cent. of morphia.

Morphia, when obtained from its alcoholic solution, is in small brilliant and colorless crystals: they are generally six-sided prisms, with dihedral terminations, but their form is a right rhombic prism. When gently heated they become opaque and lose water: at a higher temperature morphia fuses into a yellow liquid, which becomes white and crystalline on concreting. In the air it burns with a bright resinous flame. When heated in a close tube it yields ammonia. Morphia, though apparently nearly insoluble in cold water, has a bitter taste: boiling water dissolves not more than a hundredth of its weight, but the solution is alkaline to delicate tests. It dissolves in 40 parts of cold, and 30 of boiling anhydrous alcohol. It is almost insoluble in ether and benzole, and is only sparingly dissolved by chloroform; hence the method of separating it from narcotina, which is readily soluble in that menstruum. Morphia is soluble in potassa and soda; hence the necessity of avoiding the use of these alkalies in its precipitation. Ammonia dissolves it sparingly, so that this alkali ought not to be used in excess.

Much has been said respecting the methods of detecting morphia by tests: those which are commonly resorted to are *nitric acid*, which when dropped upon crystallized morphia, forms a bright-red solution; and *neutral perchloride of iron*, which produces a very characteristic blue color (or blue-green), when added to morphia, or to its salts, provided the solutions are not very dilute. *Iodic acid* is, according to Serullas, the best test of the presence of morphia; it produces a reddish-brown color, and the odor of iodine is immediately perceptible. The minutest quantity of morphia has the property of decomposing iodic acid, but in cases where very small quantities are present, it is recommended that a solution of starch should be employed to detect the free iodine.

CODEIA ($C_{35}H_{20}O_5N+2HO$).

This alkaloid was discovered by Robiquet, in 1832, in the hydrochlorate of morphia. On dissolving the mixed hydrochlorates in water, and precipitating the morphia by ammonia, the codeia remains in solution and crystallizes by subsequent evaporation: it may be also separated by ether, in which it is soluble. According to Pelletier, 100 pounds of opium yield 6 ounces of codeia.

Codeia crystallizes in acicular, or flat prisms, colorless and transparent. It fuses without decomposition, when heated in a tube to about 300°, and the mass crystallizes on cooling. In the air it burns away with a smoky flame. Water at 60° dissolves 1·26 per cent., and at 212°, 5·9 per cent. When it is present in larger proportions than the boiling water can dissolve, the excess fuses, and remains at the bottom of the solution. Its solution is sensibly alkaline to tests. Codeia is soluble in alcohol and in ether, and in the dilute acids, and forms distinct and easily crystallizable salts. It is distinguished from morphia, by its greater solubility in water and in ether, by its insolubility in fixed alkalies, by its not being reddened by nitric acid, nor blued by perchloride of iron.

Narceia ($C_{28}H_{20}O_{12}N$). *Thebaia* ($C_{25}H_{14}O_3N$), *Papaverine* ($C_{40}H_{21}O_8N$), and *Meconine* ($C_{10}H_5O_4$), are other crystalline principles found in opium.

NARCOTINA ($C_{48}H_{24}O_{15}N$).

This well-defined and distinct principle appears to exist in opium in a free state: it may be obtained from powdered opium by digesting it in warm ether, which takes up little else than narcotina, and yields it in crystals. When caustic potassa is added to an aqueous solution of opium, so as just to saturate the free acid, the matter which falls consists chiefly of resin and narcotine. When all the soluble parts of opium have been extracted by water, as in making extract of opium, and in the preparation of morphia, the residue, digested in dilute hydrochloric acid, also yields narcotina.

Narcotina is insipid when pure. It fuses at 268°, and when slowly cooled concretes into a crystalline mass. It is deposited from its alcoholic or ethereal solution in well-defined rhombic prisms, insoluble in cold, and sparingly soluble in hot water; 100 parts of boiling alcohol (sp. gr. 0·825) dissolve about 5 parts of narcotina, 4 of which crystallize on cooling: boiling ether dissolves about 3 or 4 per cent., of which it deposits more than one-half, on cooling. It is soluble in the volatile and fat oils, but insoluble in alkaline solutions. It does not render a solution of a persalt of iron blue, nor is it reddened by nitric acid. This acid turns it yellow. Sulphuric acid, containing a mere trace of nitric acid, immediately reddens it most intensely: but when mixed with pure sulphuric acid, it acquires a yellow color. A particle of an alkaline nitrate added to the mixture brings out a blood-red color. It does not decompose iodic acid. Heated on paper over a candle, it produces a greasy-looking stain. As it does not affect vegetable colors, it is easily distinguished from morphia and codeia. It is readily soluble in dilute acids, forming salts which are very bitter, and with difficulty obtained in the crystalline state, for when evaporated they are mostly decomposed into acid and narcotina, and crystals of the latter only separate. This is especially the case with the acetate of narcotina, and furnishes a means of separating it from morphia, for the latter substance is retained in permanent combination and solution.

Cinchonia. *Cinchonine* $(C_{20}H_{12}ON = \overset{+}{C}in)$.

This alkaloid is obtained from the principal varieties of pale or gray Peruvian bark. It is usually in the form of white semi-transparent crystals, requiring about 2500 parts of water at 212° for their solution, and are almost insoluble in cold water. They have little taste, but become intensely bitter upon the addition of almost any acid. They restore the blue color of reddened litmus. They are sparingly soluble in cold alcohol, ether, and fixed oils; but more abundantly soluble in boiling alcohol: the solution deposits crystals on cooling, and becomes milky when dropped into water. It forms with acids a large number of salts.

Quinia. *Quinine* $(C_{20}H_{12}O_2N, = \overset{+}{Q})$.

Quinia is generally obtained from *yellow bark.* It almost always contains more or less cinchonia: these alkaloids may be separated by solution in alcohol, which, when duly evaporated, deposits the cinchonia in crystals, while the quinia, being more soluble, remains in solution: by one or more repetitions of this process, it may be freed from cinchonia. If they are converted into *sulphates*, the sulphate of quinia, being less soluble than the sulphate of cinchonia, crystallizes, and leaves the latter salt in solution. Sulphate of quinia, which is abundantly prepared for medicinal use, is the most ready source of the alkaloid: it is obtained by adding ammonia to a solution of that salt, when it falls in white flakes, which unless very carefully dried, are apt to become brown. Quinia is very difficult of crystallization, but it has been obtained in crystals by slowly evaporating its alcoholic solution by exposure to cold dry air.

Quinia has a decided alkaline action; it is intensely bitter; very sparingly soluble, even in boiling water, of which it requires about 200 parts for its solution. It is readily soluble in boiling alcohol, and the solution, when evaporated, leaves it in the form of a viscid mass, which indurates and acquires a resinous aspect on exposure to air. It is more soluble than cinchonia in chloroform and ether. It forms distinct salts with the acids. When anhydrous quinia is heated in a tube, it fuses, becomes thick, viscid, and dark-colored, an oily liquid evaporates, ammoniacal and hydrocyanic vapors follow, and a bulky carbonaceous matter remains.

The *Salts of quinia* are for the most part crystallizable, and are generally less soluble in water, and more bitter than the salts of cinchonia; they are also soluble in alcohol. The aqueous solution has a peculiar bluish opaline appearance, as a result of *fluorescence*. They are liable to acquire a yellow or brown tint by long exposure to solar light. In this altered state they form the substance called *quinoidine*—a mixture of several basic compounds, including *quinidine* ($C_{40}H_{24}O_4N_2+4HO$), isomeric with quinine. It is extracted by ether. These different bases of Peruvian bark are combined in the plant with a peculiar crystallizable acid, called the Cinchonic or Kinic acid ($C_7H_5O_5,HO$).

STRYCHNIA ($C_{44}H_{24}O_4N_2$).

The following is Merck's process for the extraction of this alkaloid. The seeds of nux vomica are boiled for 24 or 36 hours in a closed boiler, with water enough to cover them, acidulated by one-eighth of its weight of sulphuric acid; they are then bruised and beaten into a paste, and the liquor well expressed. Excess of caustic lime is then added to it, and the precipitate, having been pressed, is boiled in alcohol of sp. gr. ·850, and filtered hot; strychnia and brucia are deposited together in a colored and impure state, and may be separated by cold alcohol, which dissolves the brucia. The remaining strychnia is then boiled in alcohol with a little animal charcoal, and the solution filtered boiling hot; on cooling, the strychnia crystallizes. The same process is applicable to the Ignatius' beans.

Strychnia is a powerful poison, destroying life in the dose of half a grain. It is a white crystalline solid, neither fusible nor volatile, but easily decomposed by heat, yielding ammonia, in close vessels. It requires 7000 parts of cold and 2500 of boiling water for solution: the intensity of its bitterness is such, that an aqueous solution which does not contain more than a forty-thousandth of its weight of strychnia is sensibly bitter. It is soluble in common alcohol, especially at its boiling temperature, and readily crystallizes in quadrangular prisms and octahedra from this solution. Absolute alcohol and ether scarcely dissolve it when quite free from acid. It is dissolved by chloroform and benzole, and separated from water by these solvents when an alkali is added to a solution of a salt of strychnia. It is dissolved by the acids, forming colorless and crystallizable salts. It is not soluble in the alkalies. Nitric acid does not color strychnia or its salts, if free from brucia; but it frequently reddens them, owing to the presence of traces of brucia.

When a minute quantity of strychnia is moistened with a drop of concentrated sulphuric acid, the strychnia is dissolved without any peculiar color, but if a minute quantity of the peroxide of lead or manganese, of bichromate of potassa, or ferricyanide of potassium, is added, a fine blue tint is developed, which passes into violet and red, and after some hours into a pale yellow color. This reaction is characteristic of strychnia. The peroxide of manganese in small quantity is preferable for this experiment. A strong solution of strychnia gives crystalline precipitates with sulphocyanide and ferricyanide of potassium. The latter when touched with sulphuric acid, develops the colors. (HORSLEY.)

This alkaloid perfectly neutralizes the acids, and forms soluble and very bitter and poisonous salts: they are mostly crystallizable. The caustic alkalies throw down from their solutions a white precipitate of strychnia, which may be dissolved and removed by agitating the liquid with twice its bulk of ether or chloroform. This is the process usually pursued for the extraction of strychnia in cases of poisoning. The liquid is acidulated, concentrated in a water-bath, rendered alkaline by potassa, and then shaken with two volumes of ether. The ethereal liquid poured off, and spontaneously evaporated, leaves strychnia. The salts of strychnia are precipitated by tincture of galls.

BRUCIA ($C_{44}H_{25}O_7N_2$).

This alkaloid is most abundantly procured from the bark of the *Strychnos nux-vomica*, commonly called *false angustura.* This bark is coarsely powdered, and, having been previously digested in ether to free it from fatty matter, is treated by alcohol, the alcoholic solution evaporated, and the residue dissolved in water saturated with oxalic acid, and evaporated to dryness. Alcohol digested upon this residuum dissolves coloring matter, and leaves pure *oxalate of brucia*, which may be decomposed by lime, and the brucia dissolved out by boiling alcohol, from which, by slow evaporation, it is obtained in crystals.

Brucia forms either prismatic or foliated crystals, according as it has been slowly or rapidly deposited: it is soluble in about 850 parts of cold, and in 500 of boiling water. Sometimes, on precipitating a salt of brucia by ammonia, the alkaloid separates in the form of an oil, which after a time concretes, if left in contact with water. The taste of brucia is strongly and permanently bitter: its poisonous action resembles that of strychnia, but it has only one-sixth of the power. It is very soluble in alcohol, but insoluble in ether, and in the fat oils: it is sparingly soluble in essential oils. It forms soluble salts with the acids, which are mostly crystallizable; they are bitter, and are decomposed not only by the alkalies, but by morphia and strychnia, both of which precipitate the brucia. Brucia is strongly reddened by nitric acid, and the color changes to violet when the liquid is warmed and protochloride of tin added. It is distinguished from strychnia by its not producing the blue and purple colors when mixed with sulphuric acid and peroxide of manganese.

Strychnia and brucia as they exist in the vegetable structure, are combined with a peculiar acid, called the strychnic or igasuric.

VERATRIA ($C_3H_{22}O_6N$).

This alkaloid is contained in the seeds of the *Veratrum sabadilla*, and in the roots of the *Veratrum album*, or *white hellebore*, united with gallic acid. Commercial veratria is not crystallizable; it has a pungent but not a bitter taste, and powerfully irritates the nostrils, causing the most violent sneezing. A small dose produces nausea and vomiting. It is a powerful poison. It fuses at a temperature of 122°, and concretes, on cooling, into a translucent yellow mass. Boiling water does not take up more than a thousandth part of its weight, but it is readily soluble in alcohol, and somewhat less so in ether. Chloroform dissolves it in large quantity. Veratria is characterized by its producing, when warmed with diluted sulphuric acid, an intense crimson color.

COLCHICIA. *Colchicina.*

This substance, originally confounded with veratria, has been shown by Geiger and Hesse, to exist in the *Colchicum autumnale,* as a distinct alkaloid, but it has not been analyzed, nor has its atomic weight been determined. It exists in the bulb and flowers gathered in July, but is best obtained from the pulverized seed, which is digested in alcohol acidulated by sulphuric acid; lime is then added to the liquor, which is filtered, saturated by sulphuric acid, and the alcohol expelled by distillation. The remaining concentrated aqueous solution having been decomposed by excess of carbonate of potassa, the precipitate is dried and digested in absolute alcohol. The alcoholic solution of the alkaloid is then decolored by animal charcoal, filtered, and gently evaporated: the product is afterwards purified by repeated crystallizations.

Colchicia is a powerful poison. It crystallizes in colorless needles which have a bitter taste and are very poisonous; it causes purging and vomiting in very small doses. It is slightly alkaline and easily fusible. It is rendered deep blue by concentrated nitric acid, becoming afterwards olive-colored and yellow; sulphuric acid renders it brown. It is soluble in water, alcohol, and ether, and its aqueous solution is precipitated by tincture of iodine, by solution of platinum, and by infusion of galls. It neutralizes the acids, and forms salts which are mostly crystallizable, permanent in the air, and very bitter and acrid. They are soluble in water and alcohol, and their aqueous solutions are acted upon by reagents similarly to colchicia. When not too dilute, the alkalies precipitate the alkaloid.

ATROPIA. HYOSCYAMIA. DATURIA. PICROTOXIA.

Atropia is the poisonous alkaloid of the Atropa Belladonna, or Deadly nightshade; *Hyoscyamia*, of the Hyoscyamus niger; *Daturia*, of the Datura Stramonium, and *Picrotoxia* of Cocculus Indicus. *Aconitina* and *Digitalia* are extracted respectively from Aconitum napellus and Digitalis purpurea. These alkaloids are all active poisons. Their composition has not been accurately determined. There are other alkaloids of less interest, which require no particular notice in a chemical point of view.

The bases hitherto considered contain oxygen. There are two volatile alkaloidal bodies, Nicotina and Conia, which contain no oxygen.

NICOTINA ($C_{10}H_8N$).

Nicotina is obtained by boiling dry tobacco leaves in water acidulated by sulphuric acid, and evaporating the decoction; the residue, digested in alcohol, yields a solution of sulphate of nicotina, which, when concentrated and distilled with quicklime, furnishes a solution of ammonia and nicotina. Ether abstracts nicotina from this solution, and when a sufficiently concentrated ethereal solution has been thus obtained, it must be deprived of water by agitation with chloride of calcium, decanted, and distilled; the nicotina remains in the retort.

Pure nicotina is a colorless, limpid, oleaginous liquid, having a slight odor of stale tobacco; when it contains ammonia, this odor is very intense. At a temperature below 475° it may be slowly distilled, but at that temperature it is decomposed; its sp. gr. is 1·048. It is powerfully alkaline to test-papers; it is very inflammable, and burns with a smoky flame. When dissolved in water, caustic potassa separates it in the form of oily drops. Ether abstracts it from its aqueous solution. It dissolves in all proportions in alcohol and in oils. It is decomposed when heated with hydrate of potassa. Exposed to air it becomes brown and resinous: it is decomposed by chlorine, iodine, and nitric acid. It is eminently poisonous, but does not occasion dilatation of the pupil: half a drop killed a rabbit; one drop was fatal to a dog; a tenth of a grain applied to the eye of a cat, occasioned violent convulsions and paralysis of the hind-legs, which lasted for an hour. Nicotina neutralizes the acids and forms difficultly crystallizable salts, which are very soluble in water and alcohol. When it is slightly supersaturated by hydrochloric acid, nicotina gives no precipitate with bichloride of platinum, but the mixture, after some hours, deposits acicular crystals. If the nicotina contains ammonia, it occasions an immediate precipitate. The solution of nicotina produces a white precipitate with corrosive sublimate.

CONIA. *Conicina* ($C_{16}H_{16}N$).

It appears from the experiments which have been made upon hemlock, that its active principle resides in a volatile and uncrystallizable alkaloid; its properties have been investigated by Geiger, and by Dr. Christison (*Edin. Phil. Trans.*, 1836, p. 383). When the seeds or leaves of hemlock are distilled with water, the fluid which passes over has the odor of the plant, but is not poisonous; but when caustic lime or potassa is previously added to the green seeds or leaves, and these are distilled with water at as low a temperature as possible, the liquid which then passes over is both alkaline and poisonous. When 10 or 12 ℔s of the seeds are worked at once, an oily matter comes over at first, which is nearly pure conia, but the greater part of the alkaloid is dissolved in the distilled water; if this be redistilled, it loses a little of its strength; but if previously neutralized by an acid, such as the sulphuric, the poisonous principle becomes fixed, and water alone distils over. The residue consists of sulphate of conia, sulphate of ammonia, and resin, the latter being produced by the decomposition of part of the conia. To obtain the conia, the above residue is digested in a mixture of 2 parts of alcohol and 1 of ether, which leaves the sulphate of ammonia; and then, the alcohol and ether being carefully distilled off, the remaining sulphate of conia is heated gently with a little water and caustic potassa, when there is obtained in the receiver a watery solution of conia in the lower part, and floating on this, a layer of nearly pure hydrate of conia, containing a trace of ammonia; the water may be abstracted by chloride of calcium, and the ammonia by exposure *in vacuo.*

Conia thus obtained has the appearance of a colorless volatile oil, lighter than water, of a powerful diffusible color, somewhat like that of hemlock, and when diluted resembling the smell of mice: it is intensely acrid to the taste. It has a strong alkaline action on reddened litmus and on turmeric. It is readily soluble in diluted acids, which it neutralizes, but its salts have not been crystallized. It is sparingly soluble in water, and combines with about a fourth of its weight of water to form a hydrate.

Conia is a deadly poison to all animals: it first palsies the voluntary muscles, then the respiratory muscles and the diaphragm, thus producing death by asphyxia. The heart continues to act after other signs of life are extinct. Few poisons equal it in subtlety or swiftness; a drop put into the eye of a rabbit, killed it in nine minutes; three drops, in the same way, killed a strong cat in a minute and a half; two grains of conia, neutralized with hydrochloric acid, and injected into the femoral vein of a young dog, produced almost instant death: in two seconds, or three at farthest, and without the slightest warning struggle, respiration had ceased, and with it all external signs of life. If conia be present in an extract or other preparation, it may be detected by triturating either the solid or liquid with a solution of potassa, upon which the odor of mice will be strikingly perceptible.

ANILINE. *Phenylia.* ($C_{12}H_7N$).

This is an artificial base which contains no oxygen. It has been already referred to as a product of the distillation of coal. It may be procured by distilling indigo with a strong solution of potassa. It is now obtained in large quantities, for dyeing and other purposes, by distilling nitrobenzole with a mixture of acetic acid and zinc, or iron, in which case, it is decomposed by nascent hydrogen.

Aniline when pure is a colorless or oil-like liquid, possessing a very high refractive power: it has a strong disagreeable odor, and a hot aromatic flavor. It boils, according to Hofmann, at 360°, but it evaporates rapidly at common temperatures, and the greasy spot which it produces on paper quickly disappears; it remains perfectly fluid at 0°; its sp. gr. at 60° is 1·020. It is soluble to a certain extent in cold water, and the solution becomes turbid when heated; it is soluble in all proportions, in alcohol, ether, wood-spirit, aldehyde, acetone, sulphide of carbon, and in fixed and volatile oils. It has no alkaline reaction on turmeric or on reddened litmus, but it changes the violet color of dahlia-paper to green. When a glass rod dipped in hydrochloric acid is held over its aqueous solution, white fumes are produced, resembling those formed by ammonia. Aniline dissolves sulphur when aided by heat, and on cooling, deposits it in prismatic crystals; it also dissolves phosphorus, camphor, and colophony, but not copal or caoutchouc; like creasote, it coagulates albumen.

When aniline is exposed to air, it absorbs oxygen, and becomes yellow, brown, and resinous. A few drops of fuming nitric acid added to anhydrous aniline produces a fine blue color, which on slightly heating the mixture passes into yellow, and violent action ensues, sometimes followed by explosion; otherwise, the liquor passes through various hues, and crystals of picric acid are formed in it (p. 566). When aniline is added to a solution of permanganate of potassa, peroxide of manganese is thrown down, and oxalic acid and ammonia are formed. When treated with a solution of chloride of lime, a beautiful violet-blue color is produced, which is reddened by the addition of an acid; this reaction is very characteristic of aniline. When chlorine is passed into aniline, it assumes the consistence of tar, and on distilling this product, a compound passes over, composed of $C_{12}H_6NCl$. When heated with corrosive sublimate, it produces a splendid red dye. It is now largely employed in the manufacture of the coal-tar colors (p. 626).

Aniline forms a series of crystallizable salts with different acids.

The production of aniline from nitrobenzole furnishes an apt illustration of the complexity which it is proposed to introduce into chemical formulæ, in place of the simple system which is now generally employed. When nitrobenzole is distilled with a mixture of iron-filings and acetic acid, it is converted into aniline, as a result of the evolution of nascent hydrogen; and the simple equation which represents this change is:—

$$\underbrace{C_{12}H_5(NO_4)}_{\text{Nitrobenzole.}} + \underbrace{6H}_{\text{Hydrogen.}} = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + \underbrace{4HO}_{\text{Water.}}$$

The following represents the changes, according to Dr. Hofmann, on what is called the unitary system:—

$$\underbrace{(C_6H_5)NOO}_{\text{Nitrobenzole.}} + \underbrace{HH + HH + HH}_{\text{Hydrogen.}} = \underbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O}_{\text{Water.}} + \underbrace{\left.\begin{matrix}(C_6H_5)\\H\\H\end{matrix}\right\}N}_{\text{Aniline.}}$$

Emetina, Caffeine, Theine, and other Bases.

Emetina ($C_{37}H_{27}O_{10}$).—This term is applied to the active or emetic principle of *Ipecacuanha*. It is a white, inodorous, and almost insipid powder, alkaline to tests, and sparingly soluble in cold water. It is more soluble in alcohol; but ether, the essential oils, and the caustic alkalies, scarcely act upon it; it fuses at about 120°. Concentrated nitric acid converts it in the first instance into a bitter yellow resinoid substance, and ultimately into oxalic acid. It neutralizes the acids, and forms salts which are not crystallizable except with excess of acid. Emetina has a powerful emetic action. In a dose of three or four grains it acts as a poison.

Piperine ($C_{34}H_{19}O_6N$).—This substance is obtained from *black pepper*. It is generally a pale straw color, and crystallizes in the form of four-sided prisms, insoluble in cold, and slightly soluble in hot water; readily soluble in alcohol, and less so in ether. When quite pure, it is inodorous and tasteless. It fuses at a little above 212°, and is not volatile, but when more highly heated, yields ammoniacal products. It is regarded as a feeble alkaloid.

Asparagine ($C_8H_8O_6N_2+2HO$).—This principle exists in asparagus. It is best obtained from the expressed juice of asparagus, evaporated to the consistency of syrup, and set aside; it deposits crystals, which are purified by solution in water and recrystallization.

Asparagine forms transparent prismatic crystals, which are hard, brittle, of a cooling and somewhat nauseous taste, neither alkaline nor acid; soluble in 58 parts of cold water, and more soluble in hot; insoluble in anhydrous alcohol, and in ether. When asparagine is long boiled with hydrated oxide of lead, magnesia, or other bases, it is resolved into ammonia and into an acid, called *Aspartic acid.*

Caffeine. Theine. ($C_8H_5O_2N_2$). *Guaranine.* This important compound is found in coffee (the seed of *Coffea Arabica*) and in tea, the leaves of *Thea Chinensis:* it is also said to occur in the leaves of *Guarana officinalis* or *Paullinia Sorbilis*, and in *Ilex Paraguayensis* (*Paraguay tea*). It is remarkable that one and the same principle, and that belonging to the class of azotized basic bodies, should be found in two such dissimilar vegetables as tea and coffee, infusions of which are used over the greater part of the known world.

Caffeine may be procured as a crystalline sublimate in considerable quantity in the roasting of large quantities of coffee; it sublimes in an impure form, but is easily deprived of its adhering impurities. The process generally recommended for its preparation is that of Runge: it consists in making a strong aqueous infusion of ground raw coffee, adding to it a solution of sugar of lead, which occasions a green precipitate, and leaves the supernatant liquid colorless; the excess of the salt of lead in this liquid is then precipitated by sulphuretted hydrogen, it is filtered, and evaporated; the caffeine remains, and must be treated by animal charcoal to whiten it, and recrystallized.

Caffeine (or theine) forms white silky crystals, soluble in boiling water and alcohol, and deposited in crystalline filaments as these solutions cool: it has no alkaline reaction, yet it appears capable of combining definitely with some of the acids, especially with hydrochloric acid.

Theine is thus prepared: a decoction of tea is first treated with a slight excess of acetate of lead, which throws down the tannic acid and almost all the coloring matters it contains; it is then filtered whilst hot, and the clear liquid is evaporated to dryness. It forms a dark yellowish mass, which is to be intimately mixed with a quantity of sand, and introduced into Mohr's subliming apparatus and moderately heated for 10 or 12 hours. The theine sublimes in beautifully white anhydrous crystals, deposited upon the paper diaphragm which runs across the apparatus. The only point to be observed is that the temperature should never rise too high, as the more slowly the operation is conducted, the finer are the crystals and the greater their quantity. From a pound of coffee, Stenhouse obtained an average produce of 15 grains of theine, sometimes not so white as that made from tea, but rendered so by a second sublimation. From hyson tea (green), Stenhouse obtained 1·05 per cent. of theine; from Congou (black) 1·02 per cent.; from

Assam (black) 1·27, and from Tonkay (green) 0·98. But Peligot, guided by the large proportion of nitrogen evolved in the ultimate analysis of tea, was lead to suspect a larger proportion of theine, and obtained the following quantities, namely, from hyson, 2·56 to 3·40 per cent., and from gunpowder tea 2·20 to 4·10 per cent.

Theobromine ($C_{14}H_8O_4N_4$) is a base which is contained in the cocoa-nut. It is but little soluble in water, alcohol, and ether. It has a bitter taste, and forms crystallizable salts with acids.

Salicine ($C_{26}H_{18}O_{14}$).—This is a crystalline substance which is extracted from the bark of the willow. It is soluble in water and alcohol: its solutions have a bitter taste: they are lævo-gyrate with regard to polarized light. Salicine is characterized by the deep red color which is produced when the crystals are moistened with strong sulphuric acid. When salicine is boiled with dilute sulphuric acid, glucose or grape-sugar is a product. Nitric acid converts it into oxalic and carbazotic acids. When distilled with bichromate of potassa and dilute sulphuric acid, salicylous acid or hydride of salicyl ($C_{14}H_5O_4,H$) is obtained in the distillate. This is identical with the essential oil of Meadow-sweet (*Spiræa ulmaris*). Salicine yields about one-fourth of its weight of the hydride. When fused below redness with three parts of hydrate of potassa, a salicylate of the alkali is obtained, from a solution of which salicylic acid is precipitated by the addition of hydrochloric acid.

A solution of a *salicylate* is characterized by its striking a *violet*-blue color with a persalt of iron. Certain insects which feed upon willow bark, oxidize salicine in their bodies. If placed on paper impregnated with a persalt of iron, and they are irritated, they eject a liquid which produces a blue or violet-colored spot on the paper.

The oil or essence of winter-green (*Gaultheria procumbens*) is a salicylate of the oxide of methyle ($C_2H_3O+C_{14}H_5O_5$). It has a strong agreeable odor, and acquires a violet color on the addition of a persalt of iron.

Phloridzine ($C_{42}H_{24}O_{20},4HO$) is a crystallizable principle obtained from the bark of the apple and pear trees, by simply boiling the decoction in water, and allowing the liquid to cool. When boiled with diluted acids, grape-sugar is one of the products. Salicine, phloridzine, and some other principles of a similar kind, which thus yield grape-sugar, under such simple conditions, have received the name of *Glucosides.*

ORGANO-METALLIC BASES.

We have elsewhere referred to the compounds of zinc with the organic radicals methyle (p. 548), amyle (549), and ethyle (555); but there is probably no compound more remarkable for its constitution and range of combination, than that which was discovered and isolated by Bunsen under the name of *Kakodyle.*

KAKODYLE ($C_4H_6As=Kd$).—This is a compound of metallic arsenic with carbon and hydrogen: it derives its name from its highly offensive odor. Bunsen procured this radical by decomposing anhydrous chloride of kakodyle by pure zinc, and distilling the product. Owing to its spontaneous combustion in air, and its highly poisonous nature, great precautions are required in its preparation. It is a clear colorless liquid (sp. gr. 1·48), the density of its vapor being 7·2. When cooled to 20° it crystallizes in square prisms. When exposed to air, oxygen, or chlorine, it burns, forming with oxygen, water, carbonic and arsenious acids. It is resolved at a red heat into arsenic, light carburetted hydrogen, and olefiant gas; and by these results its exact constitution has been determined ($C_4H_6As=As+2CH_2+C_2H_2$).

Kakodyle, like cyanogen, combines with oxygen, sulphur and chlorine.

It also combines with cyanogen (p. 519). Oxide of kakodyle (KdO) is known under the names of *Alkarsine* and *Cadet's fuming liquor.* It is procured by distilling at a red heat, a mixture of equal weights of arsenious acid and dry acetate of potassa. The vapor has an offensive odor resembling that of garlic, and is very poisonous. The oxide is a colorless liquid (sp. gr. 1·64). It is insoluble in water, but dissolves in alcohol and ether. Another oxygen compound (KdO_3,HO) is known under the name of *Kakodylic acid* or *Alkargen.* It is procured by mixing red oxide of mercury with oxide of kakodyle under water. This acid may be obtained crystallized in prisms. Although it contains 56 per cent. of arsenic, 6 or 7 grains of it, according to Bunsen, produced no ill effects on a rabbit. The *chloride* is procured by distilling the oxide with corrosive sublimate and hydrochloric acid; and the *cyanide* by distilling the oxide with concentrated hydrocyanic acid.

The preparation of any of these compounds is attended with great danger to the operator. Bunsen states, that in distilling the oxide, an explosion is very likely to occur, if the glass bulb above the level of the liquid becomes too hot. "Should a drop of the liquid, during ebullition fall on that part, the whole of the apparatus is shattered to pieces, and an arsenical flame several feet high rises up, covering everything near it with a black offensive layer of arsenic." Of the cyanide of kadodyle he says, that "the vapor diffused in the smallest quantity through the atmosphere, produces a sudden cessation of muscular power in the hands and feet, giddiness and insensibility, which end in total unconsciousness.

CHAPTER LIV.

ORGANIC COLORING-MATTERS. DYEING.

UNDER this head a variety of substances are included, of very different character and composition. Many of them are important in the arts: they are used as pigments, and extensively employed by dyers and calico-printers. Others are of so fugitive a nature as not to admit of this application, and are chiefly known as giving variety and beauty to flowers, or as communicating to vegetables in general, those infinitely varied shades of green which characterize this division of the organic creation. By far the greater number of these substances are educts of vegetable origin, or products of the decomposition of vegetable substances. The coloring-matters derived from animal substances are comparatively few.

A colored compound is a frequent product of chemical changes in colorless organic compounds. When gallic acid is dissolved by heat in strong sulphuric acid, a rich crimson-colored liquid is produced. On dissolving essential oil of bitter almonds in the same acid, a ruby-red liquid is produced, which becomes yellow on exposure to air. Pyroxanthine gives with sulphuric acid in the cold, splendid purple and crimson compounds, which gradually darken by exposure. When crystallized cane-sugar in powder is mixed with arsenic acid and water, so as to form a thick paste, the mixture slowly acquires, by exposure to air at a temperature of about 70°, a splendid crimson color, which gradually darkens. When arsenious acid is employed no colored compound results. The substitution of aniline for sugar, and the application of heat to the mixture of aniline and arsenic acid, has been recently made the subject of various patents for the production of permanent purple dyes. The action of sulphuric acid and bichromate of potassa on strychnia and aniline, in producing blue, purple, and crimson-colored compounds, furnishes other instances of the production of splendid colors from colorless organic substances (p. 607). A small quantity of a solution of gallic acid added to lime-water produces a white precipitate, which speedily becomes blue, purple, and ultimately olive-green. Bile produces with sulphuric acid and sugar, aided by heat, a splendid purple color, and with nitric acid a rich green color. In most of these cases, it may be proved that color is produced as a result of the oxidation of the organic substance; and in reference to many of the coloring matters described in this chapter, it will be found that they do not exist ready formed in the living plant, but are products of the oxidation of certain principles contained in the sap or vegetable fibre. Chemical compounds which impart oxygen, *e.g.*, chromic acid, the peroxides of manganese and lead, and arsenic acid, produce color; while those which have reducing properties, such as nascent hydrogen, sulphuretted hydrogen, alkaline sulphides, and the protoxides of manganese and iron, render the colored compounds temporarily colorless. Organic colors are easily destroyed by exposure to light. This, which is called fading, may be due to the effect of nascent oxygen or ozone. That nascent oxygen has a powerfully destructive influence, is seen in the action of ozone, and of chlorine. Humid chlorine completely destroys all organic colors (p. 174). Sulphurous acid also bleaches them either by removing oxygen, or by forming with the coloring matter, colorless compounds, which are soluble in water, and admit of removal by washing. Acids and alkalies sometimes restore the color when sulphurous acid has been used, but not when chlorine has been employed (p. 201).

Some coloring principles, although neutral in reaction, appear to act like acids in combining with bases. Thus alumina and the oxides of tin and iron, form insoluble compounds with organic colors, and at the same time modify the color. Hydrate of alumina precipitates most organic colors which are soluble in water, rendering the liquid colorless. Charcoal in powder has a similar effect: it removes the color without altering it (p. 241). Animal and vegetable fibres also remove and fix these colors by a powerful attraction, and they are sometimes employed for the purpose of separating the coloring principle in a pure state (*see* CARTHAMEINE, p. 621). As a general rule, wool appears to have the strongest attraction for coloring substances; silk comes next to it, then cotton, and lastly hemp and flax.

The art of dyeing and calico-printing consists in the application of these organic colors to animal or vegetable fibre, such as silk, wool, linen, or cotton. It is based on simple chemical principles. In the first place, the articles require to be thoroughly cleansed from all foreign matters and colors: this is effected by washing and *bleaching*. The simple operation of dyeing is generally performed upon animal fibre, such as wool and silk; whilst the more refined operation of printing in patterns and devices of various colors is chiefly, though by no means exclusively, conducted upon cotton, or, as it is usually termed, calico. Some colors are of such a nature as to combine with the fibre without any *medium;* and when this is the case, they constitute what have been termed *substantive* colors. Other colors require the intervention of a *base* or *mordant*, and they are then called *adjective* colors. The mordants which are most frequently resorted to are the salts of alumina, iron, and tin. Albumen, as well as the alkaline phosphates and arsenates, are also employed as mordants in calico-printing. The substance to be dyed, is first impregnated with the mordant, and then passed through a solution of the coloring matter, which is thus fixed in the fibre, and its tint is often modified or exalted by the operation. A considerable portion of the mordant is retained in the fibre of the calico or cloth which is dyed. Ure found that 100 parts of the ashes of Turkey-red calico (dyed by an alum mordant) afforded between 16 and 17 parts of alumina, whereas the ashes of white and washed calico afforded only a trace of that earth.

Calico-printing, which is a more refined and difficult branch of the art, is a species of topical dyeing. In this process *adjective* colors are almost always employed. The mordants, the principal of which are acetate of alumina and acetate of iron, and albumen, are first applied to the calico by means of wooden blocks or copperplates, or cylinders, upon which the requisite patterns are engraved. When albumen is used as a mordant, this is fixed by exposure to a steam-heat. The stuff is then passed through the coloring bath, and afterwards exposed on the bleaching-ground, or washed. The color flies from those parts which have not received the mordant, and is permanently retained on those parts to which the mordant has been applied. A variety of colors is produced by employing various mordants, and different coloring materials, and by using them in various states of dilution and combination. Instead of first applying the mordant, and afterwards the coloring material, they are occasionally both printed together, but in these cases particular management is requisite in the selection of the substances employed, and in the mode of their application: when this method is resorted to, the color is often *fixed* by the application of steam. Thus in the employment of albumen, either of egg or blood, or of lactarine (the curd of cheese), the coloring-matter is at once mixed with the organic principle, and the colored compound is printed in a pattern on the cloth. When the cloth has been subjected to the steaming process, the color and the albumen mixed with it are rendered insoluble, and remain fixed on the fibres of the stuff. Cottons, which receive dyes with more difficulty than silk or wool, are thus effectually dyed. By the aid of albumen or lactarine, insoluble mineral colors, such as ultramarine, or Scheele's green, may be imprinted on the finest fabrics.

We shall here consider the principal coloring matters which are employed in chemistry and the arts.

INDIGO.—Indigo, as it occurs in commerce, is usually in the form of cubical pieces, or cakes, friable, and more or less brittle, and of various shades of a peculiar deep blue. When rubbed with a hard body, it acquires, like Prussian blue, a coppery-red color, but always furnishes a deep-blue powder; it is tasteless, nearly inodorous, and almost insoluble in water, alcohol, and ether. The masses of indigo have a dull conchoidal fracture, and the finest samples are those which are lightest and most copper-colored. The plants resorted to as a source of indigo, are different species of *Indigofera;* it is also obtained from other genera, as *Nerium*, *Isatis*, *Marsdenia*, *Polygonum*, and *Asclepias*. Indigo appears to exist in the juices of these plants, in the form of a colorless soluble compound; and it is generally obtained by fermenting the bruised plant, during which ammonia is evolved, and a yellow liquid obtained. This liquid, on the addition of lime-water, and exposure to air, deposits the blue indigo in the form of a flocculent precipitate. Its chief sources are India and South America.

INDIGO-BLUE. *Indigotine* ($C_{16}H_5O_2N$).—It is this coloring matter which gives the commercial value to indigo, of which it forms about 50° per cent. In order to obtain the pure coloring principle, the indigo of commerce is sccessively treated with hydrochloric acid, weak solution of potassa, and hot alcohol, to remove any foreign substances. It is then thoroughly mixed with twice its weight of freshly-slaked lime, and the mixture put into a bottle capable of holding 150 times the quantity of indigo operated on; the bottle is then filled with boiling-hot water, and 4 parts of crystallized protosulphate of iron added for every 3 of indigo; it is then securely stopped so as to be air-tight, and having been well shaken, is set aside for several hours. In this way the indigo-blue, which is insoluble, is converted into *indigo-white*, which is soluble in the solution of lime, producing a yellow liquid. This yellow liquor is then poured off, mixed with dilute hydrochloric acid, and left for a long time exposed to air; the acid retains the lime and other substances in solution, while the indigo-blue is deposited, and may be freed from hydrochloric acid and chloride of calcium, by washing with water.

Indigotine is volatile, without decomposition, at a low temperature. If powdered indigo is carefully heated in a tube through which a current of hydrogen is passing, the indigotine sublimes in a violet-colored vapor resembling that of iodine, and is deposited in purple crystals in the form of fine needles. If over-heated, or heated in air, it is decomposed. The sublimation takes place readily at about 550°: the melting-point of this substance, its point of volatilization, and that at which it is decomposed, are very near to each other. The sp. gr. of sublimed indigo-blue is 1·35. When the crystals are heated in an open vessel, they sublime without residue, in a reddish-violet vapor; in close vessels, as the heat advances, the vapor acquires a scarlet tinge, and then becomes orange colored; a small quantity and of aniline is formed, and charcoal is deposited.

Heated upon platinum-foil, indigo-blue gives a purple smoke, and if the heat be rapidly augmented it fuses, boils, and burns with a bright flame, giving off much smoke, and leaving a carbonaceous residue, which may be entirely consumed. Indigo-blue is insipid and inodorous, and neither basic nor acid. It is insoluble in water, alcohol, ether, and the oils. Dilute acids and alkaline solutions have no action upon it.

INDIGO-WHITE. *Indigogene* ($C_{16}H_6O_2N$).—If the yellow solution, obtained by the action of lime and protosulphate of iron upon indigo and water, is decomposed by an acid under the cautious exclusion of oxygen, a white precipitate is formed: this is indigo-white. It may be obtained by syphoning the yellow liquor into a stopper bottle previously filled with hydrogen or carbonic acid gas, and containing some acetic or dilute hydrochloric acid, the syphon itself being previously filled with water deprived of air. Under these circumstances a white, flocculent, and often somewhat crystalline precipitate falls: it should be most carefully excluded from all contact with air, and allowed to subside; the supernatant liquor must then be decanted, the precipitate collected upon a filter in an atmosphere of hydrogen or of carbonic acid, washed with water freed from air, pressed in folds of bibulous paper, and dried *in vacuo.*

Indigo-white, when dried, has always a greenish or bluish tint, though it probably would be perfectly white, if quite pure. It has a silky fracture, is destitute of taste and odor, and shows no acid reaction. It is not volatile, and when heated *in vacuo* it gives off a little water, while indigo-blue sublimes, and carbon remains: no permanent gas is evolved. It is insoluble in pure water, and in dilute acids. It forms a yellow solution in alcohol and in ether, and these solutions, when exposed to air, gradually deposit indigo-blue. When moist, it speedily passes into indigo-blue under the influence of air; and even when dry, it slowly acquires a blue color: this change goes on even *in vacuo*, in consequence probably of the air retained in the pores of the substance being sufficient to communicate to it a blue tinge. When it is gradually heated in air, the whole mass suddenly acquires a dark-purple color, being converted into indigo-blue.

Although a neutral principle, indigo-white acts in the manner of an acid in respect to bases. It forms yellow solutions with the alkalies and alkaline earths, which, when exposed to air, become immediately covered with an iridescent copper-colored film of indigo-blue, whilst the liquid underneath acquires at first a peculiar reddish-green tint, and then gradually passes into blue. Hence the liquid containing it, is an admirable test for free oxygen, either as a gas, or as it is contained in water.

Indigo-white was originally regarded as deoxidized indigo, or as a lower oxide of the base of indigo-blue; the processes, therefore, by which indigo-white is obtained, were considered as cases of deoxidation, and it was supposed that simple oxidation was the cause of the change of the white into the blue oxide. But Dumas has shown that in passing into white indigo, blue indigo acquires an additional atom of hydrogen, the proportion of oxygen remaining the same in both (*see* p. 501).

SULPHINDIGOTIC ACID; *Sulphindylic Acid* ($[C_{16}H_4O_2N+S_2O_5]+HO$).—When 1 part of indigo-blue is digested for 3 days with 15 parts of oil of vitriol, in a stopped bottle, at a temperature between 120° and 140°, a deep blue solution is obtained, without any evolution of sulphurous acid. This solution mixes perfectly with water, and if the preceding proportions have been adhered to, there is no sediment; it is a solution of *sulphindigotic acid.* The Nordhausen or Saxon sulphuric acid forms a better solvent than common oil of vitriol. When evaporated to dryness, the acid remains in the form of a dark blue substance, which is deliquescent, and has a peculiar odor; it forms a dark blue solution with water and alcohol, of a sour and somewhat astringent taste. If woollen cloth be immersed in the diluted blue liquor, it becomes effectually dyed, and the liquid is entirely deprived of color. By digesting the blue wool in a solution of carbonate of ammonia, a solution of *sulphindigotate of ammonia* is obtained, with which several other salts of the blue acid may be prepared.

When zinc or iron is put into the aqueous solution of this acid, it loses its color, but regains it by long exposure to air. Sulphuretted hydrogen does not affect it at common temperatures; but when heated to 120°, sulphur is thrown down, and the blue color disappears. Protochloride of tin, and all those substances which convert indigo-blue into indigo-white, act similarly upon this acid. When protosulphate of iron is dissolved in a solution of a neutral sulphindigotate, the color is not destroyed, nor is it affected when part of the oxide of iron is thrown down by an alkali, but the moment that the whole of the oxide is precipitated and an excess of alkali is present, decoloration ensues; on again adding an excess of acid, the blue color returns.

Sulphopurpuric Acid ($[C_{32}H_{10}O_4N_2+2SO_3]+HO$).—When 1 part of indigo is triturated with 7 or 8 parts of oil of vitriol (or better, with fuming sulphuric acid), the mixture, upon the addition of water, deposits sulphopurpuric acid in the form of a purple powder, which must be immediately washed upon a strainer with water acidulated by hydrochloric acid, until all traces of free sulphuric acid are removed, and then carefully dried *in vacuo.* This acid is soluble in pure water and in alcohol. By digestion in oil of vitriol, it passes into the sulphindigotic acid. It saturates only 1 atom of base.

Isatine ($C_{16}H_5O_4N$).—This compound is the result of the oxidation of indigo by chromic or nitric acid. A dilute aqueous solution of chromic acid is gradually added to pulverized indigo; the mixture is heated nearly, but not quite, to its boiling-point, and a brown solution is obtained. The chromic acid should only be of such strength as freely to dissolve the indigo; if it is too strong, carbonic acid is evolved, oxide of chromium is precipitated, and isatine is not formed. The brown solution should be filtered whilst hot, and the isatine crystallizes as the liquor cools.

Isatine forms brilliant reddish-brown prismatic crystals, inodorous, sparingly soluble in cold, but more abundantly in hot water, and readily soluble in alcohol, but less so in ether. The alcoholic solution communicates a peculiarly unpleasant and permanent odor to the cuticle. When isatine is heated in a tube, a portion of it sublimes, but the greater part is decomposed, leaving carbon, which is with difficulty combustible. Heated in air it fuses, exhales a suffocating vapor, burns with a brilliant flame, and leaves a carbonaceous residue. By the action of chlorine and bromine, it forms *chlorisatine*, *bichlorsatine*, *bromisatine*, and *bibromisatine*. It dissolves in solutions of ammonia, potassa, sulphuretted hydrogen, and sulphide of ammonium, producing peculiar compounds. Isatine may be regarded as indigo +2 atoms of oxygen; or $C_{16}H_5O_2N+O_2$. *Isatinic acid* ($C_{16}H_6O_5N+HO$) is procured by the action of a solution of potassa upon isatine.

Isatyde ($C_{16}H_6O_4N$) is a white crystalline compound which may be obtained by adding a little sulphide of ammonium to a hot alcoholic solution of isatine in a close vessel.

Aniline and *Picric acid* are also products of the decomposition of indigo by potassa and nitric acid. These compounds are elsewhere described (pp. 566, 610).

Lichen-blues. Archil; Litmus.—These substances are prepared from various *lichens*, amongst which *Rocella tinctoria* and *corallina*, *Lecanora Tartarea*, *Variolaria lactea* and *dealbata* have been especially resorted to. The lichens are principally collected from rocks adjoining the sea: they grow abundantly on the Canary and Cape Verd Islands; and there is a general similarity in the mode of treating them for the manufacture of the above mentioned colors. They are cleaned, and ground into a pulp with water; ammoniacal liquids, derived chiefly from gas-works, or occasionally from urine, are from time to time added, and the mass is frequently stirred so as to expose it as much as possible to the action of air. Peculiar substances existing in the lichens are, during this process, oxidized by the joint action of air and water, in the presence of ammonia, thereby generating the coloring matter. When the color is extracted, the mass is pressed, and chalk, plaster of Paris, or alumina, is added, so as to form it into a consistent paste. In this state, it is of a purple or violet-red tint, and constitutes the *archil* of commerce, frequently called *Cudbear* (from Cuthbert, one of the manufacturers of the article at Leith); it is the *orseille* and *persio* of the French and Germans. The other variety is called *litmus*, or in France and Germany, *tournesol* and *lacmus*, is generally made up into small cubes, and has a fine violet color. The lichens which are proper for the manufacture of these colors, may be recognized by moistening them with a little solution of ammonia, and setting the mass aside in a corked phial; if of the proper kind, the lichen and the liquid will acquire a purple tint in the course of a few days.

The following substances have been discovered in these coloring principles.

Lecanorine; Lecanoric or *Orsellinic Acid* ($C_{18}H_8O_8+HO$).—This compound exists in different species of *lecanora*. It is obtained by exhausting the lichen with ether, which is then distilled off, and leaves a residue containing lecanoric acid, mixed with resinous and fatty matter, and some substances soluble in water. Lecanoric acid forms inodorous and tasteless stellated groups of silky acicular crystals, insoluble in water, but soluble in hot alcohol and ether. Subjected to dry distillation, it is resolved into *orcine* and carbonic acid; and it undergoes the same change when moistened with sulphuric acid and left in a damp place; or when boiled in a solution of ammonia or potassa.

$$\text{1 atom of lecanoric acid, } C_{18}H_8O_8 = \begin{cases} \text{1 atom of orcine} \;\; . \;\; . & C_{16}H_8O_4 \\ \text{2 \quad `` \quad carbonic acid} & C_2 \;\; O_4 \end{cases} \qquad \overline{C_{18}H_8O_8}$$

Orcine ($C_{16}H_8O_4+HO$).—This substance is one of the principal sources of the coloring-matter derived from lichens. It is found ready formed in *Lichen roccella, parellus, deustus, tartarius, dealbatus,* &c., and is produced by various processes from lecanorine. It is obtained by exhausting the dried and pulverized lichen in boiling alcohol, and filtering while hot. The alcoholic extract dissolved in water, deposits long brown brittle needles, which may be redissolved in water, treated with animal charcoal, filtered, and again crystallized.

Orcine crystallizes in flat four-sided prisms, with dihedral summits; it has a sweet but somewhat repulsive taste, and it is perfectly neutral. When dried at 212°, it loses a portion of its water of crystallization; at about 550°, it rises in vapor, may be distilled, and condensed in crystals, which contain 1 atom of water. It is soluble in water and in alcohol.

If orcine is exposed to air, it gradually reddens, especially when the sun occasionally shines upon it. When subjected to the action of chlorine, it heats, fuses, and hydrochloric acid is produced. Nitric acid acts upon orcine with the evolution of nitrous gas, and a red solution is formed, which deposits a resin-like substance. The fixed alkalies convert it into a brown substance. Gaseous ammonia is absorbed by orcine, and on exposure to air it again escapes; but when water is present, the oxygen of the atmosphere is absorbed, and a colored azotized body is the result, to which the name of *orcêine* or *orcêic acid* has been given.

Orcêine; Orcêic Acid ($C_{16}H_8O_6N,+HO$).—This substance may be obtained by placing pulverized orcine in a capsule, together with a saucer of solution of ammonia, under a bell-glass; the orcine becomes brown, but on exposure to air the excess of ammonia escapes, and on adding a little water, and a few drops of ammonia, a purple liquid is obtained, from which acetic acid throws down *orcêine,* or, as Berzelius terms it, *orcêic acid.* Sulphuretted hydrogen docolors the purple liquid, not by deoxidation, but by entering into combination with orcéic acid, for the color reappears on exposure to air, or on saturating the sulphuretted hydrogen by an alkali. A solution of litmus, when kept in a close-stopped vessel for some time, acquires a dirty-brown color, and smells offensively. When exposed to air, it rapidly assumes a purple and blue color. In the preparation of blues from lichens, orcéic acid is produced under the influence of ammonia. It is not itself a permanent dye-stuff, but is a valuable auxiliary in the production of other blues and purples.

Erythrine; Erythryline; Erythric Acid ($C_{20}H_{14}O_{10}$).—These are probably identical with, or, at all events, closely related to, lecanorine.

Litmus-paper.—The lichen blues are much used for the preparation of litmus-paper. In order to prepare this paper for chemical purposes, an ounce of litmus, finely powdered, should be infused in half a pint of boiling water in a covered vessel for an hour. The clear liquor should then be poured off, and fresh quantities of hot water added until the color is exhausted. White, unsized paper, containing but little mineral matter, cut into convenient lengths, should then be dipped into the infusion and allowed to dry. It should have a full blue color. Paper thus prepared, if not tinted of too deep a color, forms the best tests for acids, either gaseous or liquid. It is sooner or later reddened. Red litmus-paper forms a very delicate test for alkalies, as the blue color is restored by alkaline liquids. In order to prepare it, the blue litmus-paper should be exposed in a jar to the diluted vapor of acetic acid or humid carbonic acid. In order to act with delicacy as a test for an alkali, the reddish tint thus artificially imparted to it, should be barely perceptible. These test-papers should be cut in strips of three inches by half an inch, and kept in well-stopped bottles in a dark closet. Light destroys the color, and exposure to air reddens the paper by the action of carbonic acid and other acid vapors diffused through the atmosphere. A paper prepared from an infusion of the best cudbear, without the addition of either alkali or acid, has a purple color, and is affected both by acids and alkalies; it is convenient in *alkalimetry*, being already too red to be affected by carbonic acid, while it is distinctly reddened by mineral acids.

MADDER; *Garancine; Alizarine; Alizari.*—The plant which furnishes this valuable dye-stuff (*Rubia tinctorum*) is common in the south of Europe and in many parts of the Levant, where it is known under the name of *alizari:* it is also largely cultivated in Holland. It has a long spreading fibrous root, which is the part used in dyeing. In the living plant, the sap is yellowish colored: and contains no red coloring principle. This appears to be developed in the woody fibre, during the act of drying, and by exposure to air. Madder-root contains three coloring-principles, named respectively xanthine, alizarine, and purpurine. By digesting the root repeatedly in cold water, the *xanthine*, or madder-yellow, is removed, as this principle is very soluble in water. When the residue is treated with half its weight of sulphuric acid at 212°, the woody fibre is in great part destroyed, and may be removed by further digestion with water. A brown pulverulent residue is left, which is known under the name of *garancine*. This contains a red coloring-matter, *Alizarine* ($C_{20}H_6O_6$), which may be obtained in orange-colored crystals by digesting the garancine in boiling alcohol, or by subjecting it to superheated steam. It is scarcely soluble in water, hot or cold, but is readily dissolved by alcohol and alkaline solutions. The latter change the red to a violet color. It gives a bluish precipitate with solutions of lime and baryta, thus acting like a weak acid. Sulphuric acid dissolves it, forming a brown liquid, but it is again precipitated unchanged on dilution with water.

Purpurine ($C_{18}H_6O_6$), or madder-purple, is a red coloring principle, which may be procured by digesting the washed root in a boiling saturated solution of alum, in which alizarine is insoluble. On adding sulphuric acid to the decoction, the purpurine is slowly deposited. It may be obtained as a deep red powder, by repeated digestions in alcohol and ether. It is not dissolved by cold water, but it is soluble in hot water. It is also soluble in alcohol and ether. When a solution of carbonate of soda is added to a decoction of madder-root in alum, there is an abundant precipitate of the red coloring matter with alumina, constituting what is called *madder-lake*.

CARTHAMINE. *Carthameine.*—This is the coloring principle of *Safflower*, the petals of the *Carthamus tinctorius*, or *Bastard saffron*. It is cultivated in Spain, and in many parts of the Levant, whence it is chiefly imported; but on account of its price it is seldom used, except to give the finishing hue to some silks, and in the preparation of the article called *rouge*. Safflower contains a *red* coloring-matter which is insoluble in water, and a *yellow* soluble substance. The former has been distinguished as *carthameine*, and appears to be derived from the oxidation of a peculiar principle existing in the petals, which has been called *carthamine*.

Carthamine ($C_{26}H_9O_5+2HO$), is obtained from the flowers, after all soluble matters have been extracted by water, by digesting them in a weak solution of carbonate of soda. It crystallizes in small white prismatic needles of a bitterish taste, not very soluble in water, but more soluble in alcohol; it is not volatile, but fuses when heated, exhales a pungent odor, and burns away without residue. When exposed to the air, it gradually acquires a yellow color. When an alkaline solution of carthamine is left in contact with oxygen, it becomes first yellow, and then red, and on saturating this red liquor with citric acid, red *carthaméine* is thrown down. When air is excluded, the alkaline solution remains colorless.

Carthaméine. Carthamic Acid ($C_{26}H_9O_7$).—This is the product of the oxidation of carthamine, under the influence of alkaline bases: it exists in the safflower, from which it may be extracted by digesting it, after the yellow matter has been removed by water, in a solution of carbonate of soda, and then precipitated by citric acid. It forms a dark-red powder, insoluble in water and in acids, and sparingly soluble in alcohol, to which it communicates a fine red color; it is also sparingly soluble in ether. It is not volatile, but is decomposed by dry distillation. It forms salts with the alkalies, from which it is thrown down by organic acids, of a bright rose-red color.

The affinity of carthaméine for cotton and silk is such, that when it is recently precipitated, these substances immediately combine with it, become at first rose-colored, and afterwards of a fine red, so that they may be thus dyed without the intervention of a mordant. The stuffs so dyed, are rendered yellow by alkalies, and the color is, to a certain extent, restored by acids. Carthaméine is never used in dyeing wool. When it is precipitated from concentrated solutions, it furnishes a liquid paint, which, evaporated upon saucers, leaves a residue of a somewhat greenish metallic lustre, used as a pink dye-stuff, and which, mixed with finely powdered talc, and dried, constitutes common *rouge*.

HÆMATOXYLINE. *Hæmateine.*—These substances are extracted from logwood, a dye-stuff of considerable importance: it is the heartwood of the *Hæmatoxylon Campechianum*, and is imported from Campeachy, Honduras, and Jamaica, in hard and dense logs, about three feet long, and of a dark-red or purple color. In the dye-house it is used for the production of certain *reds* and *blues*, but its chief consumption is for *blacks*, which are obtained of various intensities, by means of iron and alum bases.

Hæmatoxyline ($C_{16}H_7O_6,HO$), which has also been called *hæmatine*, is procured by digesting the aqueous extract of the wood in alcohol. The alcoholic tincture, when submitted to spontaneous evaporation, deposits crystals of this substance. An aqueous solution of these crystals, does not become colored by exposure to air, but the addition of a few drops of ammonia causes the liquid to assume an intense-red color. By this reaction the hæmatoxyline is converted into *hæmateine* ($C_{16}H_6O_6$), which may be procured in crystals of a purple-black color with a metallic lustre. The crystals dissolve in water, giving to the liquid when concentrated, a deep purple tint. This compound differs from hæmatoxyline in containing 1 atom less of hydrogen.

BRAZILINE ($C_{36}H_{14}O_{14}$) is the red-coloring principle of Brazil-wood. It may be procured in small prismatic crystals, which are soluble in water, alcohol, and ether. A decoction of the wood is of a reddish-brown color; it acquires a rich purple hue by the addition of alkalies. The coloring principle, *Braziline*, when treated with ammonia and exposed to air, is converted into a new compound, *brazileine*, which is of a deep purple color. An alcoholic solution of braziline is a delicate test for the presence of alkalies; and paper which has been dipped in a decoction of Brazil-wood and dried, is sometimes employed for this purpose. The red color given by the Brazil-wood is very fugitive.

Brazil-wood is distinguished from logwood by its paler hue, and by the precipitates which its infusion forms with acetate of lead, protochloride of tin, and lime-water: these are crimson, instead of being violet-colored as with logwood. The infusions of both woods are rendered yellow by a drop of sulphuric or hydrochloric acid. *Red ink* is usually made by boiling about two ounces of Brazil-wood in a pint of water for a quarter of an hour, and adding a little gum and alum.

SANTALINE. *Santaléine.*—Red Sanders is the name given in this country to the wood of the *Pterocarpus santalinus*, a large tree which grows upon the Coromandel coast, and in other parts of India, especially Ceylon. The coloring principle of this wood is *Santaline*, a white crystalline powder, which speedily reddens on exposure to air. It is instantly reddened by alkalies, and furnishes red solutions with the greater number of the dilute acids. It dissolves in water, alcohol, and ether, and when its aqueous solution is long boiled under exposure to air, it is converted into *santaléine*, which is a dark red crystalline substance. Its probable formula is $C_{16}H_8O_3$, but the composition of this substance and of santaline has not been accurately determined.

ANCHUSINE. *Anchusic Acid.*—These terms have been applied to the coloring matter of the root of *Alkanet* (*Anchusa tinctoria*), a species of *bugloss*, which is a native of the warmer parts of Europe, and is cultivated in our gardens. Large quantities are raised in Germany and France. *Anchusine* ($C_{17}H_{10}O_4$) has the characters of a resin; it is dark red, and of a resinous fracture, softened by heat, insoluble in water, soluble in alcohol, and very soluble in ether and in fat and volatile oils, to all which it communicates a bright red color.

LAC.—This is a resinoid substance, the production of which appears to depend upon the puncture of a small insect (the *Cocus ficus*), made for the purpose of depositing its ova, upon the branches of several plants, especially the *Ficus religiosa* and *Indica* (p. 571). The coloring matter of lac is prepared in India, and is extensively used as a scarlet dye-stuff, for the production of which it is a most efficient substitute for cochineal. Two forms of it are imported, called *lac-lake* and *lac-dye.* These substances contain about 50 per cent. of the red coloring matter, mixed with more or less of the resin, and with earthy matters, said to consist chiefly of chalk, gypsum, and sand.

COCHINEAL-RED. *Carmine.*—The substance known in commerce as *cochineal*, consists of the dried female insects of a species of coccus. It is imported from Mexico and other countries. The insects, when powdered, yield a deep reddish-black substance, which, when boiled in water, forms a dark-red solution that speedily undergoes decomposition. If to the fresh-filtered liquid a solution of alum or acid tartrate of potassa is added, a precipitate is slowly formed, which consists of the coloring principle of the insect, united to some animal matter. This is commercial *carmine.* In general the pigment is prepared by boiling cochineal in a weak solution of carbonate of potassa or soda, and adding to the filtered liquid, a solution of alum and cream of tartar. The coloring principle is then slowly precipitated with alumina, forming carmine-lake. The precipitation is sometimes accelerated by the use of gelatine or albumen. The purest form of the coloring principle is obtained by the following process: The powdered insects are boiled in ether, to separate fatty matter. They are then boiled in alcohol, until this liquid is saturated with color, and from the alcoholic decoction, the carmine is deposited on cooling. This principle is soluble in water, forming a rich red solution, which is heightened by acids, and changed to a deep red crimson by alkalies. It is also soluble in alcohol, but not in ether. A variety of carmine now prepared is scarcely dissolved by water; but when a few drops of ammonia are added, it forms a splendid red solution with a slight crimson tint. Its composition has not been accurately determined. A substance procured from cochineal by Pelletier, by a process similar to that which has been above described, is known under the name of *Carméine* or *Coccinelline* and its composition is represented as $C_{32}H_{26}O_{20}N$. *Carminic acid*, which is obtained by precipitating an aqueous decoction of cochineal by acetate of lead, and decomposing the washed precipitate by sulphuretted hydrogen, has the composition of $C_{28}H_{14}O_{16}$.

GUANO-COLORS. *Murexide* (from *Murex*, a shell-fish, the supposed source of Tyrian purple.)—This is commonly known as the purpurate of ammonia of Prout: it is an animal-red of a rich purple shade. It is procured by the reaction of nitric acid on uric acid, and has been lately largely manufactured from guano as a dye-pigment. The guano is first digested in hydrochloric acid to remove foreign substances; the residue, consisting of acid and sand, is treated with soda; this dissolves out the uric acid, which may now be readily procured by neutralizing the liquids with hydrochloric acid. Nitric acid converts uric acid, in the cold, into alloxan; and dilute nitric acid heated, converts it into alloxantine. When uric acid is dissolved in nitric acid of a sp. gr. of 1·40, and the solution is heated, the color is brought out by adding to the acid liquid when cold, ammonia or its carbonate, until a slight ammoniacal odor is imparted to it. Dr. Gregory advises that seven parts of alloxan and 4 parts of alloxantine should be dissolved in 240 parts of boiling water, and this solution added while hot to 80 parts of a cold saturated solution of carbonate of ammonia. The liquid becomes opaque, owing to the intense purple color produced, and crystals of murexide are deposited on cooling.

The crystals are square prisms. Like rosaniline, carthamine, and some other reds, they have a rich green color like that of beetles' wings by reflected, but are purple-red by transmitted light. They are but slightly soluble in cold water, which, however, acquires a strong color; they are soluble in boiling water, and are insoluble in alcohol and ether. The color is destroyed by ammonia and sulphuretted hydrogen. Potassa dissolves murexide, forming a rich purple solution, but the color is destroyed on boiling. When to this colorless solution, an excess of dilute sulphuric acid is added, *murexan* is precipitated. This is considered to be identical with *uramile* and the *purpuric acid* of Dr. Prout.

A solution of murexide is precipitated by the solutions of various metallic salts. In dyeing silk with murexide, corrosive sublimate is used as a mordant; in dyeing cotton, a salt of lead, and in dyeing woollen, a double chloride of tin and ammonium.

There is no agreement among chemists respecting the formula of murexide; and the discrepancies which exist appear to be at present utterly irreconcilable. The chemical changes which take place in its production cannot be represented, therefore, by any correct equation.

The vegetables which afford the different shades of *yellow* used as pigments, and in the arts of dyeing and calico-printing, are very numerous, but definite crystallizable principles have been only in a few instances obtained from them.

ANNOTTO.—This substance is derived from the pulp of the seeds of the

Bixa Orellana, a shrub which is native in South America, but cultivated in Guiana and St. Domingo, and also in the East Indies. It is usually met with in a pasty form, of a deep orange-red color, nearly tasteless, and of a disagreeable odor. It is but little soluble in water, but alcohol and ether act upon it more readily, forming solutions, which, when evaporated, leave the coloring-matter in the state of powder. It is soluble in the alkalies and their carbonates, forming dark-red liquids, in which the acids occasion orange-red precipitates. Annotto contains a yellow and a red coloring-matter; the former soluble in water and in alcohol, and slightly soluble in ether, and giving a yellow dye to silk and wool mordanted with alumina; the latter little soluble in water, but soluble in alcohol and ether, as well as in the alkalies, and rendered blue by sulphuric acid. Annotto is chiefly used as a dye for silk, giving various shades of orange. The color which it imparts is less affected by soap, acids, and chlorine, than most other similar dyeing materials, but it does not well resist the joint agency of light and air. In Gloucestershire and Cheshire it is used to color cheese, and sometimes butter and milk. It is employed as a color in varnishes.

QUERCITRINE.—This is the coloring principle of the inner bark of *quercitron* (*Quercus nigra* or *tinctoria*). It may be obtained from the aqueous decoction of the bark. It has a sweetish-bitter taste, and is soluble in water, alcohol, and ether. On exposing its aqueous solution to air, it becomes deep yellow and deposits a yellow precipitate: if this solution is boiled in a shallow basin, it becomes turbid, and deposits a quantity of yellow acicular crystals of *quercitrêine*. Quercitrine forms yellow solutions with the dilute mineral acids. With the alkalies, its solution, if exposed to air, is dark brownish-yellow. With acetate of lead the precipitate is white, and may be dried without change of color, provided air is excluded. According to Preisser, the formula of quercitrine is $C_{32}H_{15}O_{14}$; and that of *quercitrêine*, when dried at 212°, $C_{32}H_{17}O_{20}$. A decoction of quercitron bark deprived of its tannic acid, by a little gelatin, produces a fine yellow upon fabrics mordanted with alumina, and various shades of olive with iron mordants. It is much used in calico-printing.

FUSTIC.—This dye-stuff is the wood of the *Morus tinctoria*, a large tree which grows in Brazil, Jamaica, and most of the West Indian Islands. When a concentrated decoction of fustic cools, it deposits a yellow crystalline matter, to which Chevreul has given the name of *morine*.

WELD.—This, which is the *gaude* or *vaude* of the French, consists of the dried leaves and stem of the *Reseda luteola*, a plant indigenous in Britain and other parts of Europe. The whole herb is gathered when in seed, at which period its dyeing power is greatest. There are two kinds of weld, the cultivated and the wild; the former is richest in coloring matter. The decoction of this plant has a slightly acid reaction and a greenish-yellow color, which is deepened by alkalies, and rendered paler by dilute acids. It contains a coloring principle called *luteoline*.

PERSIAN BERRIES.—Under this name, the berries of the *Rhamnus tinctoria* are known amongst painters and calico-printers. They contain a coloring principle called *rhamnine*. This is obtained from an ethereal tincture of the berries. It is an almost colorless crystalline powder, of a bitter taste, and soluble in water, alcohol, and ether. These solutions soon acquire a yellow color by exposure to air, the rhamnine passing into *rhamnêine*. Nitric and chromic acids, bichromate of potassa, and other oxidizing agents, immediately produce the same change; and under the influence of alkalies, the liquids acquire, on exposure, a dark-brown color.

Chrysorhamnine, or *Rhamnëine*, and *Xanthorhamnine*, are yellow coloring principles, also obtained from these berries.

TURMERIC.—This is the root of the *Curcuma longa*, a plant which is a native of the East Indies, and much cultivated about Calcutta, and in all parts of Bengal; also in China and Cochin-China. The tubers of this plant, commonly called *turmeric*, contain a coloring principle called *curcumine*. It is obtained by treating the watery extract of turmeric by boiling alcohol of sp. gr. 0·80, and evaporating the filtered tincture. The residue is digested in hot ether: this dissolves the curcumine, which is deposited, on the evaporation of the ether, in the form of an inodorous, transparent, reddish substance, not crystalline, and acquiring a fine yellow color when rubbed to powder. It fuses at 105°, and is scarcely soluble, even in hot water, but readily soluble in alcohol and ether, and in fat and volatile oils. It therefore approaches in its characters to the resins.

Turmeric paper for chemical use is best prepared with a strong tincture of turmeric in proof-spirit.

EUXANTHINE. A substance under the name of *Purree*, or *Indian yellow*, is imported from India and China; its origin has not been well ascertained, but it is supposed by Stenhouse to be the juice of some unknown plant, mixed with magnesia. It has an odor somewhat resembling that of castor, and was therefore suspected to be of animal origin, add derived, perhaps, from the gall of the elephant or camel. The crystallizable principle which it contains, and which may be conveniently termed *euxanthine* (LÖWIG, i. 888), may be separated by boiling the crude purree in water, and treating the residue, which is of a fine yellow color (*euxanthate of magnesia*), with hot dilute hydrochloric acid. The euxanthine crystallizes as the liquid cools, and may be purified by dissolving the washed crystals in alcohol, and recrystallizing. Euxanthine is readily soluble in ammonia, potassa, and soda, forming yellow solutions, which yield crystalline compounds, soluble in water, but insoluble in solutions of the alkaline carbonates. When euxanthine is dissolved in a hot solution of carbonate of ammonia, potassa, or soda, carbonic acid escapes, and crystalline *euxanthates* are formed. These salts are soluble in alcohol. Euxanthine has the composition of $C_{42}H_{18}O_{22}$.

COAL-TAR COLORS.—The use of many of the coloring matters described in the preceding pages, has been in a great measure superseded by the discovery of various simple methods of producing almost every variety of color, in its highest perfection, from the tarry oils obtained in the distillation of coal. These discoveries are among the most remarkable of modern chemistry. We can here only advert to them in general terms. The gaseous and liquid products of the destructive distillation of coal have been already referred to, (p. 254). Although coal itself is simply a compound of five elements, C.H. O.N.S., yet, according to the mode in which it is treated, the gaseous and liquid substances obtained from it, amount to no fewer than fifty-one, some of these having a most complex composition. *Aniline* is found among them, but the quantity contained in coal-tar oil is too small, to render its extraction for the manufacture of colors practically available. In addition to aniline, the tarry-oils contain *benzole* (p. 564) and *phenole* or carbolic acid (p. 564), which are the principal substances employed in this manufacture. They may be separated from the other products by fractional distillation, and from each other by chemical processes.

Aniline-purple. Mauve.—Among the various methods of procuring *aniline-purple* may be mentioned that adopted by Messrs. Dale, of Manchester. Their process is based upon the fact that salts of aniline, when heated with a solution of chloride of copper, completely reduce it to the state of subchloride, with the simultaneous formation of a black precipitate, containing aniline-purple. One equivalent of a neutral salt of aniline is dissolved in water, and boiled for several hours with six equivalents of chloride of copper, a mixture of alkaline chlorides and copper salts being employed for this purpose. When the reaction is completed, the mixture is filtered, the black precipitate well washed and dried, and afterwards digested repeatedly in dilute alcohol, in order to dissolve out the coloring-matter, which it contains in a remarkably pure state. By heating anhydrous hydrochlorate of aniline with nitrate of lead to 360°, a bronze-like brittle mass is obtained, which contains aniline red mixed with aniline-purple. The red may be separated from the purple by boiling water; one grain of it will strongly color a gallon of water. These coloring-matters are fixed on cotton by a new mordant; the goods are prepared with a solution of the color and tannic acid, and are then passed through a bath containing tartar emetic. The tannate of antimony produced, serves to fix the dye.

By methods already described, *benzole* is easily converted into nitrobenzole, and this product into aniline (p. 520). When bichromate of potassa is added to a mixture of aniline and sulphuric acid (sulphate of aniline), a splendid purple dye is produced, which may be procured as a dark-red colored solid. When dissolved in water, this substance forms a dye of a rich purple color, known under the name of *Mauve* or aniline purple. This important discovery was made by Mr. Perkins. Aniline-purple is not very soluble in cold water, but it is dissolved more readily by hot water, or by water slightly acidulated. It is thrown down from its solution by alkalies. It is decomposed and destroyed by strong nitric acid and chlorine. Alcohol dissolves it, and its tinctorial power is said to be such, that one-tenth of a grain of the solid dye will form a rich violet-colored solution with a gallon of alcohol (Hofmann). The exact constitution of aniline-purple is not known. It forms insoluble blue and purple precipitates with corrosive sublimate and tannic acid. Tannic acid is used as a mordant for fixing the dye on cotton, the aniline-purple being dissolved in acidulated water. In calico-printing, the color is mixed with gum and fixed by albumen, according to the method already described (p. 616). Wool and silk are readily dyed by an aqueous solution without a mordant, at a temperature of about 120°.

Aniline-red. Magenta.—Aniline yields red colors with various chemical reagents. Thus, when mixed with sulphuric acid and treated with peroxide of lead, it yields a rose-colored compound, which has been called *Roseine;* and when heated with bichloride of tin, corrosive sublimate, nitrate of mercury, arsenic acid, or indigo, it produces a crimson compound, known under the name of *Fuchsine.* The production of color from a colorless organic compound, is remarkably shown in the reaction of corrosive sublimate on aniline. The white mineral solid and the aniline form by mixture a colorless paste: but when this is heated, it acquires an intense crimson color. From this colored product, which appears to be a salt, Mr. Nicholson succeeded in procuring a colorless crystalline body, *Rosaniline* ($C_{20}H_{21}N_3O$), which acts the part of a base, and which, on entering into combination with acids at a moderate heat, produces the well-known crimson dye (*Magenta*). The salts of rosaniline may be obtained on evaporation, perfectly crystalline. The acetate crystallizes in splendid octahedral crystals, which have by reflected light the metallic greenish color of beetles' wings; but when dissolved in water, they form a solution of an intense crimson color. Silk and woollen readily take this dye, without the aid of a mordant. Cotton and linen require to be mordanted with albumen. When aniline is heated with bichloride of tin to a high temperature in a close vessel, a rich *blue* dye is produced, which is known under the name of *Bleu de Paris.*

The colors which are obtained by these processes, depend on the oxidation of aniline, and they vary with the degree of oxidation. Thus the same ingredients yield a violet, purple, or red color, according to the proportions in which they are used. Mr. Price found that aniline-red (roseine) was produced by boiling together, 1 equivalent of aniline, 1 equivalent of sulphuric acid, and 2 equivalents of peroxide of lead; and aniline purple (purpurine) was the product, when 2 equivalents of aniline, 2 equivalents of sulphuric acid, and 1 equivalent of peroxide of lead were employed. The redness of the tint appears to increase with the degree of oxidation. According to Girard, 10 parts of aniline, added to a mixture of 12 parts of arsenic acid in 12 parts of water, gradually heated to about 248° and not above 320°, yield a rich aniline-red with a slight violet tint. When the same quantity of aniline is used with 24 parts of arsenic acid in 24 parts of water, an aniline purple or violet color is obtained. Of all the processes yet suggested, it appears that there is none which, for economy and perfection of color, surpasses that originally devised by Mr. Perkins. In this, the oxidation of aniline is effected by bichromate of potassa. The selection of a proper mordant materially affects the results. Of all the mordants yet proposed for the aniline dyes, the stannate of soda appears to be the most efficient.

A *yellow* dye is obtained by the reaction of strong nitric acid on phenole or carbolic acid (*see* p. 564). The product is *picric* or *carbazotic acid,* the properties of which have already been described (p. 766). Silk, when impregnated with alum, acquires a rich yellow color by immersion in a solution of this acid. Various shades of *green* may be obtained by the admixture of the yellow of picric acid, with indigo, and other blues.

Coloring-matter of Flowers.—These are principally *blue,* (*Anthocyanine*); *red,* (*Antherythrine;* and *yellow,* (*Anthoxanthine*): they have as yet been imperfectly examined; many of them are very fugitive, change considerably in tint, and are often altogether destroyed, on drying; others are comparatively permanent. According to Thompson, the expressed juice of most red flowers is blue, whence he infers that the coloring-matter in the petals is reddened by carbonic acid, which escapes on exposure. The violet is colored by a blue matter which is changed to red by acids, and first to green, and then to yellow by alkalies, the green probably resulting from the mixture of blue and yellow. The petals of the red rose, when triturated with a little chalk and water, yield a blue liquid which is rendered green by alkalies and their carbonates, and restored to red by acids. The same blue coloring-matter as that of the violet, exists in many other flowers, and seems also to form the most usual *red* of the red flowers, in which it is apparently reddened by an acid, for many of these reds become blue when cautiously neutralized by an alkali, and green and yellow by an excess of alkali. This is also the case with the red of the red cabbage and of the radish. Some of these reds become blue merely on being bruised, and give blue infusions with water. The color of yellow flowers is generally more permanent than that of the blue or red; it is rendered paler by acids, and deeper by alkalies. Most of the coloring-matters of the petals of flowers, are extremely susceptible of the bleaching influence of sulphurous acid and chlorine. The coloring-matter of yellow flowers, is partly soluble and partly insoluble in water and spirit. The red petals of *Papaver rhœas* yield a red solution with lime-water or carbonate of soda; potassa renders it green, and hydrochloric acid pale red: the color of red rose-leaves is brightened by acids, and rendered green by alkalies.

COLORING-MATTER OF LEAVES. *Chlorophylline. Xanthophylline. Erythrophylline.*—*Chlorophylline* ($C_{18}H_9O_8N$), from which leaves and herbage derive their green color, may be procured by digesting the crushed leaves in renewed portions of ether; this tincture is then evaporated on a water-bath, and the deposit which is formed, is separated, dried, and digested in alcohol so long as any green soluble matter is abstracted. Chlorophylline appears as a dark-green earthy substance, which is grass-green when reduced to powder. It fuses at about 390°. When moist, it is slightly soluble in alcohol, with a grass-green color; when dry, it is less soluble, and the color of the solution is bluish-green. It is similarly soluble in ether, and it communicates a green color to oil of turpentine and to fat oils. It is insoluble in water. When the ethereal solution of chlorophylline is long exposed to light, it acquires a yellow color, and on evaporation, leaves a residue having all the characters of *xanthophylline.*

Xanthophylline is a term applied to the coloring-matter extracted from the *yellow leaves* which fall in autumn. It was obtained from the leaves of a pear-tree by Berzelius, by digesting them for several days in a bottle entirely filled with alcohol of sp. gr. 0·833, and well stopped, so as to exclude air; for when it is in contact with the leaves under these circumstances, they change from yellow to brown. On distilling off the alcohol from the tincture thus prepared, and allowing the residue to cool slowly, the xanthophylline, together with a little resinous and fatty matter, is deposited. It is a dark-yellow substance, fusible at about 110°, and becoming transparent on cooling; it is insoluble in water, sparingly soluble in alcohol, and readily soluble in ether.

Erythrophylline.—It has been remarked by Berzelius, that all trees and shrubs, the leaves of which redden in autumn, bear red fruit or berries. (*Sorbus aucuparia*, *Prunus cerasus*, *Ribes grossularia*, &c.) He obtained this red coloring-matter from cherry and red-currant leaves, by digesting them, when in a proper condition, in alcohol, and distilling the red tincture. The changes of color which the leaves of many forest-trees undergo in autumn, passing from green to red, and from red to yellow, have been ascribed by Macaire-Prinsep to the action of certain chemical agents upon a single coloring-matter. (*Ann. Ch. et Ph.*, xxxviii. 415.) But L. Gmelin has remarked, that chlorophylline is not rendered yellow by acids, nor xanthophylline red: and the properties of chlorophylline appear to show that it is not in itself susceptible of such changes of color.

CHAPTER LV.

NEUTRAL NITROGENOUS SUBSTANCES. THE SOLID CONSTITUENTS OF THE ANIMAL BODY, AND SUBSTANCES DERIVED FROM THEM.

NEUTRAL nitrogenous substances are found in the vegetable and animal kingdoms: in the former they are represented by gluten, albumen, casein, or legumin: and in the latter by fibrin, albumen, casein, and gelatin. In addition to carbon, hydrogen, and oxygen, they all contain nitrogen, and the greater number contain variable quantities of sulphur and phosphorus: animal gelatin contains neither of these elements. These principles are important as articles of food to animals, and they are frequently described as *flesh-forming* substances, in order to distinguish them from the neutral compounds of the three elements C.H.O., starch, gum, and sugar, which, according to modern theory, are only *heat-producing.* Although their elementary composition is well known, yet as they form no definite combinations with other bodies, no correct rational formulæ have yet been constructed to represent their constitution. There is no material difference in the composition of these substances, whether they are derived from the vegetable or the animal. It has been suggested that, with the exception of gelatin, they are derivatives from a common principle, to which the name of *protein* is given (πρωτεύω, *to take the first place*) ; and that this consists of a definite number of atoms of carbon, hydrogen, oxygen, and nitrogen : hence they are generally described as proteinaceous substances. Their centesimal composition, as furnished by the combustion-tube, is given in the following table. From this it will be perceived, that the differences in elementary constitution are slight, and that differences in properties are probably due to molecular arrangement.

	Albumen.	Emulsin.	Casein.	Legumin.	Gluten.	Fibrin.	Protein.
Carbon .	54·8	50·9	54·9	50·7	55·2	54·6	55·0
Hydrogen	7·1	6·8	7·1	6·8	7·5	6·9	6·9
Oxygen .	21·2	23·4	22·2	24·9	21·4	22·8	22·0
Nitrogen .	16·9	18·9	15·8	17·6	15·9	15·7	16·1

In the above analyses, the sulphur and phosphorus are in included in the amount of oxygen. The proportion of sulphur and phosphorus, according to Mulder and Scherer, is on an average about 1 per cent. : in seralbumen, it was found to be 1·1 ; in ovalbumen, 0·82 ; and in the fibrin of ox-blood, it varied from 1·31 to 1·59 per cent. In casein, the proportion is less than in albumen. Owing to their complex constitution, and as a result of the loose attraction of their elements out of the living body, these principles, when exposed in a moist state to air at a proper temperature, undergo spontaneous changes, and are ultimately converted into *water*, *ammonia*, *carbonic acid*, and other inorganic compounds. In the stage of transition, noxious and offensive effluvia, consisting of compounds of nitrogen, sulphur, and phosphorus, with hydrogen, are evolved ; and to this stage the term *putrefaction* is applied. The conditions necessary for this process are the following :—

1. *Temperature.*—Putrefaction occurs at any temperature above 50°. That which is most favorable, varies from 70° to 100°. It most probably acts by increasing the affinity of the elements for each other. Too high a temperature coagulates or dries the substance, and thus arrests decomposition, while too low a temperature also prevents it. The greater number of animal substances may be indefinitely preserved at or below the freezing-point, and when slowly thawed, they generally regain their original characters: it is in this way that supplies of animal food are kept in a fresh state, in many parts of the north of Europe, and that fish is preserved for the London market. A remarkable instance of the preservative power of cold, was exhibited in the discovery of an ancient elephant, in a mass of ice, at the mouth of the River Lena, in Siberia. (*Mém. Imp. Acad. St. Petersb.*, and *Quart. Journ. of Science*, &c., viii. 95.) The Laplanders preserve reindeer's milk in a frozen state, and when thawed, after the lapse of several months, it perfectly retains its original characters.

2. *Moisture* is a condition essential to putrefaction. When flesh is carefully and thoroughly dried, either by a current of warm and dry air, or by other methods which do not alter its composition, it resists decay. It has thus occasionally happened that corpses have been preserved for long periods by accidental desiccation ; and animal substances which are either naturally

dry, or rendered so by art, retain their nutritive powers, and resume their former appearance when cautiously moistened. The various forms of gelatin and albumen, when desiccated are imperishable; whilst in aqueous solution, or in their original humid state, they are the most perishable of all animal proximate principles.

3. *Air*, or at least *oxygen*, if not absolutely essential to, is a powerful promoter of putrefactive changes, and, under certain circumstances, its exclusion indefinitely retards them. Hence, the rapidity of putrefaction in pure oxygen; and its retardation in gases, which either do not contain oxygen, or in which it is held by superior attractive power. Thus, in deutoxide of nitrogen, which contains more than half its weight of oxygen in an intimately combined state, and which absorbs all free oxygen brought in contact with it, we have kept pieces of beef perfectly fresh, in one experiment for 126, and in another experiment for 224 days. Even under water, when oxygen is strictly excluded, putrefaction is greatly retarded, and modified in its results. Meat immersed in water previously boiled to expel air, and then covered by a layer of oil, to prevent its subsequent absorption, may long be kept fresh.

In the putrefaction of animal matter, if there is not a sufficient supply of air to oxidize the products, ammonia and sulphuretted hydrogen abound. Thus, in bodies buried in coffins, we have found these products even after six years' interment. If water has had access to the body, a singular change takes place. The flesh and all the organs become sodden, white, and unctuous to the touch, and the soft parts are so coherent, that although the animal substance is preserved, the organs can no longer be recognized. On boiling this white substance in water a large quantity of oil rises to the surface, and ammonia escapes: the oily matter solidifies on cooling. This substance has been called *adipocire*, from its supposed resemblance to a mixture of wax and fat; and its formation has been ascribed to the reaction of ammonia, evolved during putrefaction, on the fatty acids, whereby a soap of margarate, stearate, and oleate of ammonia is produced (p. 574). We have examined a body thus metamorphosed, after eight years' burial. The result was that, while the fatty parts of the body had undergone this change, the muscular tissue still preserved a fibrous character. It was simply altered fibrin, in which the ordinary course of decomposition had been modified, by constant immersion in water and want of free access of air.

In the process for the preservation of animal and vegetable food, the substances are heated and hermetically sealed in tin canisters, the included oxygen is converted into carbonic acid, or enters into other combinations. The partially boiled or roasted meat (free from any tainted portions), with half-dressed vegetables, and soup, are introduced into a canister, which is then soldered up, with the exception of a small hole left in the lid: the canister is placed in a saline bath, heated to a few degrees above the boiling-point of water, and when steam is copiously issuing from the aperture, it is dexterously soldered up, so that the canister is not only hermetically sealed, but a vacuum is created within it: it should be strong enough to resist atmospheric pressure. The success of the process is indicated by the ends of the canister, when sealed, being concave, as a result of atmospheric pressure. When the substances have undergone putrefaction, owing to the failure of the process, the ends of the canister bulge out, if the gases produced cannot escape. In 1846 we examined one of the canisters that had formed part of the stores of the *Blonde* frigate, which was despatched to the Sandwich Islands in 1826, and circumnavigated the globe. Although twenty years had elapsed, the contents were found good and wholesome: they were readily consumed by persons who were not aware of the long time during which they had been preserved. We have another canister from the same ship still in our possession. Oil, butter, suet, and such substances, are sometimes effectual as preservatives of food; and potted meats, when covered with a film of fatty matter, which is not prone to change, are thus preserved from the contact of air.

For the preservation of animal substances for scientific purposes, we have found the following solution, recommended by Mr. Goadby, to be very efficacious: bay-salt, 4 ounces; alum, 2 ounces; corrosive sublimate, 2 grains; water, 1 quart. The preparation should be first well soaked in a portion of the liquid, and then transferred to a vessel containing a fresh solution filtered. We have preserved in this liquid for upwards of twelve years, the entire body of a bird, as well as hen's eggs deprived of their shells by immersion in dilute acetic acid.

Various chemical liquids have been recommended as *antiseptics*. For the purposes of embalming, solutions of arsenic and chloride of zinc have been used. Carbolic acid combined with an alkali has been found to possess strongly preservative properties (p. 564); but its offensive odor is adverse to its employment for anatomical purposes.

ALBUMEN.

This term is applied to an organic principle wich is soluble in cold water, but when its solution is heated to about 160°, it becomes more or less opaque, and deposits white flakes, or if concentrated, forms a coagulum; and when thus coagulated, it is insoluble in water. It is the most widely diffused of all the principles in the animal body. It exists as a *liquid* in lymph, chyle, milk, and in the blood, of which it forms about 7 per cent., in the salivary and pancreatic fluids, the humors of the eye and the brain. In certain forms of disease it is found in the bile and urine. As a *solid* it is a constituent of skin, of the brain, nerves, glands, and cellular membrane, and it is the chief component of horn, hair, nail, feathers, wool, flannel and silk. Albumen occurs in solution in the sap or juices of most vegetables, as of the potato, carrot, turnip, cabbage, asparagus, &c.; it is a constituent of the seeds of the cereal grasses, and of almonds, filberts, and most of the oily nuts; it abounds in the juice of the common houseleek, and in the shoots of young plants. The properties of albumen are best studied in the white of egg (ovalbumen), or in the serum of the blood (seralbumen), so that we shall first consider its characters as derived from these sources, and afterwards advert to its existence in other animal and vegetable products, where it is found both in the liquid and solid state.

Ovalbumen.—The albumen of the white of egg is contained in a delicate membranous texture (*oönin*), from which it may be separated by agitation or trituration with three or 4 parts of water, when the cellular membrane is gradually deposited, and the albumen remains in solution. It is difficult to obtain it in a clear solution unless it is very dilute, in which case it passes the filter: a drop or two of caustic potassa added to the white of egg dissolves the membrane, and then the solution may be more easily filtered. When carefully dried by a gentle heat, or by evaporation *in vacuo*, in a vessel containing chloride of calcium, ovalbumen is obtained in the form of a brittle transparent yellow substance, inodorous, insipid, and when triturated with cold water, resuming its original glairiness. When heated, it exhales the usual products of azotized organic bodies, and a residue of carbon remains, which is very difficult of incineration. It leaves about 6 or 7 per cent. of saline matter, composed of carbonate, phosphate, and sulphate of soda, phosphate of lime, and chloride of sodium, with traces of potassa and magnesia. 100 parts of ovalbumen, when evaporated *in vacuo*, leave a residue of from 10 to 15 parts of albumen and salts. Direct experiment shows that in the white of egg (*globulin*), the solids amount, on an average, to 12 per cent.; and in the yelk (*vitellin*)to 37·1 per cent. In the latter there is a large quantity of yellow oil containing phosphorus, which appears to give color to the yelk. This oil may be removed by alcohol or ether.

The following Table, based on direct experiments, shows the solid contents of the principal albuminous liquids in 100 parts :—

	White of egg.	Yelk.	Serum (blood).	Serum (milk).	Serum (Anasarca).
Sp. gr.	1·041		1·030	1·027	1·009
Dry organic matter	10·8	35·1	7·0	4·5	1·1
Ash	1·2	2·0	2·0	1·1	0·6
Water	88·0	62·9	91·0	94.4	98·3
	100·0	100·0	100·0	100·0	100·0

Seralbumen.—The albumen of the serum of blood resembles that of white of egg; in reference to chemical properties, they may be considered as identical. They are both slightly alkaline, and are miscible with water in all proportions. When evaporated to dryness at a low temperature, reduced to powder, and digested in cold water, the albumen of serum is difficult of solution, unless a small quantity of potassa or soda is added.

A moderately strong aqueous *solution* of albumen (white of egg, or serum) is without taste or odor: it is adhesive, and when dried in a streak on paper, it presents a varnished surface. Like a solution of gum (arabine), it exerts a left-handed rotation on polarized light. It is insoluble in and precipitated by alcohol. It appears to be converted into coagulated or solid albumen by this reagent, as it is no longer soluble in water. *Heat.*—When the solution is heated to about 150° it becomes opalescent, and at about 170° it coagulates, forming a white, translucent, and somewhat elastic substance, with which we are familiar in a hard-boiled egg; and when in this state, it is cautiously dried, it no longer remains soluble in water, but becomes tough and horny; so that there is this characteristic distinction between albumen which has, and that which has not undergone previous coagulation. As this coagulation ensues in close as well as in open vessels, it may be concluded that the proportion of water in the recent and in the concrete albumen is the same. Two parts of white of egg and one of water entirely coagulate when duly heated, but equal parts remain, under the same circumstances, semifluid; a mixture of 1 part of white of egg and 10 of water becomes opaque, but is not coagulated; and milkiness is perceptible when the white of egg forms only a thousandth part of the heated solution. Hence, *heat* furnishes the best test for the detection of this principle. Albumen thus coagulated, has the chemical properties of fibrin. When a new-laid egg is immersed in boiling water, the white does not so readily coagulate as in an old egg, a distinction, perhaps depending upon the egg having, in the latter case, lost a portion of water by evaporation through the shell, and being therefore in a somewhat less dilute state than in the fresh egg. When dilute albumen is boiled, it coagulates and, though heavier than water, becomes blended with air, and forms a scum, which rises to the surface, and is effectively used in the clarification of certain liquids.

The cause of the coagulation of albumen by heat has not been explained. "It is," says Dumas, "probably a simple isomeric modification of this body, analogous to that by which cyanic acid is converted into cyanuric acid; so that it would be interesting to determine whether the atomic weight of coagulated albumen, is not double or triple that which belongs to liquid albumen" (p. 574). When coagulated albumen is boiled in water for several hours, it becomes horny, communicating to the water traces of organic and saline matters.

Acids.—A clear aqueous solution of serum or of white of egg may be neutralized by acetic acid, without coagulation; hence it is inferred that the solubility of albumen does not depend on the presence of free alkali. Among vegetable acids the acetic, tartaric, oxalic, and gallic acids have no action upon the solution; but it is precipitated in an insoluble form by tannic acid (tannate of albumen). When a moderately strong solution is boiled with acetic acid, it is not coagulated; but a gelatinous compound results, which dissolves in an excess of acetic acid and water.

An acetic solution of albumen is precipitated by sulphuric, nitric, and hydrochloric acids, as well as by a solution of ferrocyanide of potassium. It is also precipitated slowly in the cold, but rapidly, when warmed, by solutions of neutral salts, *e. g.*, chloride of sodium, nitrate of potassa, and sulphate of soda. It is remarkable that the solutions of these salts have no action on a solution of albumen, and do not prevent its coagulation by heat; but when acetic acid is present, albumen is thrown down, at even a low temperature, in an insoluble form.

It is probable that by some chemical change analogous to this, soluble is converted into insoluble albumen in the living body. All that is required is the presence of a free acid (lactic, acetic, or hydrochloric) and chloride of sodium. A temperature of 98°, which would not alone suffice for the transformation, would in the presence of these substances, bring about the conversion.

It is less easy to explain the metamorphosis of soluble into insoluble albumen, during the process of incubation. The temperature to which the egg of the hen is submitted at intervals for a period of three weeks, is about 104°. Having examined a freshly laid egg, and another which had reached the 22d day of incubation, we found the following differences: in the recent egg the albumen was entirely soluble in cold water, and on incineration, iron and phosphate of lime were found both in the albumen of the white and the yelk. In the incubated egg, there was a perfectly developed chicken, the albumen of the yelk being contained within its abdomen. The soluble albumen of the white, had assumed the insoluble condition, and existed in the form of feathers, beak, claws, cellular membrane, and of the soft organs generally, the blood retaining a portion in the liquid state. There was no difference in the amount of iron and phosphate of lime. The shell was thinner and more brittle. The metamorphosis cannot be explained on purely chemical principles. These might show how one form of albumen passes into another; but no chemical theory can account for the conversion of one portion of insoluble albumen into feathers, and another portion into cellular membrane. We have here an illustration of *organization*, or the arrangement of matter, not according to physical and chemical laws, but by a force wholly different from them. Boerhaave, writing in 1727, says, in reference to this subject: "All the parts of a chick—as the blood, flesh, bones, &c.—are formed out of the bare white of egg; for nothing but this is consumed during the time of incubation of the hen, the yolk all the while remaining entire." The results of incubation show that soluble is not only converted into insoluble albumen, but that it is convertible into fibrin, as muscular fibre is formed, and into gelatinous tissue, as it exists in the bones of the chicken.

Concentrated sulphuric acid precipitates an aqueous solution of albumen immediately, but redissolves the precipitate. Hydrochloric acid acts in a similar manner; when these acids are diluted, no immediate precipitate ensues; but after some hours there is a white flocculent deposit.

Albumen, even in the coagulated state, like other protein-compounds, dissolves slowly in concentrated hydrochloric acid, at a boiling temperature, forming a reddish or purple liquid. When albumen has been thrown down by hydrochloric acid, it generally becomes reddish after washing and exposure to the air. This tint is somewhat characteristic of the varieties of albumen; quill, horn, &c., exhibit it when boiled in the strong acid; almonds, cocoanut, chestnuts, and other substances containing vegetable albumen, become similarly tinted.

Nitric acid is the most effectual precipitant of albumen, and is generally employed as a test for its presence. Even in a diluted state, it throws down a white precipitate from an aqueous solution; but this precipitate is quite soluble in a large excess of water. It may be, however, again thrown down, when strong nitric acid is added to the liquid. Phosphoric acid produces different effects on an aqueous solution of albumen, according to its state of hydration. The monohydrated acid throws it down in white flakes; the terhydrated acid, not only does not precipitate it, but redissolves the former precipitate: hence albumen serves as a test to distinguish these acids.

Alkalies.—Albumen is soluble in aqueous ammonia, potassa, and soda. Alcohol added to the cold potassa solution, produces no precipitate; and when the alkaline solution is boiled, the liquid becomes yellow, but the albumen is not coagulated. This alkali, even in the cold, however, alters the chemical characters of liquid albumen. Under common circumstances, acetic acid does not precipitate aqueous albumen: but when to the potassa-solution, a few drops of acetic acid are added, a dense precipitate is immediately produced. When a concentrated aqueous solution of albumen is mixed with a strong solution of caustic potassa or soda, a gelatinous compound is the result, which is soluble in water; and if this aqueous solution is evaporated at a gentle heat, pellicles like those which form on boiled milk, gradually collect upon the surface. If the strong alkaline solution is boiled, ammonia is evolved, and an alkaline sulphide is produced which blackens the salts of lead. A piece of coagulated white of egg boiled with a diluted alkaline solution of oxide of lead, speedily blackens from evolved sulphur, and in this way sulphur may be detected in quill, wool, hair, in the almond, and many other vegetable substances. Lime, baryta, and strontia form combinations with albumen, which harden on drying. The compound obtained by mixing slaked lime with white of egg, is used as a lute; it resists to a great extent the action of acid fumes.

Serum and the white of egg are coagulated by the greater number of metallic salts. Those of iron, copper, lead, mercury, silver, and antimony yield precipitates which are compounds of albumen and the metallic oxides, hence albumen is a valuable antidote in cases of poisoning by metallic salts. The precipitate is usually soluble in an excess of serum or white of egg, and sometimes in the salt which produces it. Thus sulphate of copper readily dissolves the precipitate, which it first produces in albumen. When excess of potassa is added to a mixture of albumen and hydrated oxide of copper, a transparent solution of a splendid violet color is obtained; it may be produced by adding the alkaline solution (either potassa or soda) to a mixture of serum and solution of sulphate or acetate of copper. The oxide of copper is not reduced to the state of suboxide on boiling this liquid. The subacetate of lead is a perfect precipitant of all the forms of albumen: 1 part of fresh albumen of egg in 2000 of water, is rendered turbid by this reagent. Subnitrate of mercury is also an effectual precipitant of this principle. Corrosive sublimate is a delicate test of the presence of albumen; a liquid containing only a two-thousandth part of solid albumen is precipitated by it. The white precipitate formed, is an insoluble compound of the salt with the organic substance. Albumen, it is well known, is the antidote which is employed in this form of poisoning.

Kreasote causes a copious precipitate in solutions of albumen. They are not affected by solutions of rennet, which copiously coagulate milk. Ether rather gelatinizes than coagulates the white of egg, when the two are shaken together; after a time, a yellow liquid separates, which is not coagulated by heat, and a spongy albumen remains. When serum is similarly treated, no such precipitation ensues; the mixture separates into two portions, and the ether which floats upon the surface, holds the oil of the blood in solution.

The best tests for liquid albumen, are the application of heat, the action of nitric acid, and the use of ferrocyanide of potassium and acetic acid (p. 634).

Coagulated Albumen.—Albumen, coagulated by heat, presents itself as a white solid; it dries by exposure, to a horny-looking substance. It is in this state identical in chemical properties with horn, hair, nail, quill, wool, and tortoiseshell. It is quite insoluble in water, alcohol, and weak acids: it is dissolved by strong acids and concentrated solutions of alkalies. Acetic acid added to the alkaline solution, throws down the substance called *Protein.* The alkali is supposed to abstract sulphur and phosphorus; while a previous digestion in water, alcohol, ether, and diluted hydrochloric acid, serves to remove all soluble matters contained in the albumen. However carefully prepared, we have still found sulphur in the precipitate; and the so-called protein, appears to be nothing more than the original albuminous principle somewhat altered in its properties, by the variety of chemical processes to which it has been subjected.

When protein or its compounds are boiled in a moderately strong solution of potassa, until ammonia is no longer disengaged, and the liquid after it has cooled, is saturated by sulphuric acid, sulphate of potassa is formed, the greater part of which may be separated by crystallization. If the remaining solution is poured off and evaporated to dryness, and the residue is boiled in repeated portions of alcohol, this dissolves the organic products, and leaves sulphate of potassa: as the alcoholic solution cools; it deposits a brown oleaginous matter (*erythroprotide*), and afterwards, by spontaneous evaporation, it deposits leucine ($C_{12}H_{12}O_4N$), and retains *protide,* mixed with formate of potassa in solution. (*See* page 644.) We have here illustrated the production of protein and its derivatives, by the conversion of albumen; but these compounds may be equally obtained by treating in a similar manner, fibrin, casein, or horny tissue.

Albumen presents itself in a variety of modifications in the animal body. Under the name of *globulin,* it partly constitutes the transparent humors of the eye, including the crystalline lens. The same principle associated with coloring-matter, or hæmatosine, forms the mass of the globules of the blood. It is soluble in acetic acid and alkalies; and is precipitated when either solution is brought to a state of neutrality. *Ptyalin* is a modification of albumen existing in saliva. A remarkable property which characterizes this principle, is its power of rapidly transforming starch and dextrine into glucose or grape-sugar. If starch paste is heated for a short time to 100° with saliva, it is converted into sugar. *Pyin* is an albuminous principle found in pus; *Mucin,* in mucus; and *Echidnine,* in the viper-poison. In general, the differences are slight, but in pyin and echidnine formidable poisons are produced.

Oysters, snails, and the bodies of molluscous animals generally, are compounds of modified albumen and chondrin. An analysis of oysters shows that they consist, in 100 parts, of water, 80·11; dry organic matter (albumen and chondrin), 18·69; and of saline matter, 1·2. In the saline residue, besides chloride of sodium, traces of the iodide of sodium were found.

Vegetable Albumen. Emulsin.—Albumen in the *vegetable* kingdom is generally associated with one or more of the following principles,—gum, sugar, starch, or oil. It may be procured by macerating the succulent shoots of young plants (turnips), or bruised seeds, like those of the almond, in cold water, allowing the liquid to clear itself by subsidence, and then filtering it. The cake of the almond, after the oil has been pressed out of it, yields it abundantly. The liquid coagulates by heat, and is precipitated by nitric acid, tannic acid, and a solution of corrosive sublimate, precisely like animal albumen. It has all the properties of a weak solution of ovalbumen. It contains sulphur and nitrogen. When the pulp of almond is boiled with strong hydrochloric acid, it is reddened like ordinary albumen: when boiled in a solution of potassa holding oxide of lead, it is blackened, thereby showing the presence of sulphur. The albumen of the almond, and of some other seeds, has been called *Emulsin*, from its property of forming a white or milky emulsion in water with the oil of the seed. Emulsin is stated to differ from albumen in several points. Thus, its solution, like that of casein, is precipitated by acetic acid: it is coagulated by rennet, and is thrown down by the terhydrate of phosphoric acid, which has no action on albumen. The term *Synaptase* has been applied to emulsin by Robiquet (from *συνάπτω, adsum*) in consequence of its necessary presence in the conversion of amygdaline into hydrocyanic acid and hydride of benzoyle.

CASEIN.

This term is applied to the coagulable principle of milk, as it is this which forms cheese (*caseus*). A similar substance is occasionally found in the blood, and in the pancreatic liquids of the ox and sheep: it occurs also in vegetables. It is in a state of solution in milk, and may be procured nearly pure by coagulating well-skimmed milk heated up to 150° or 160°, by a few drops of acetic acid. The curd thus obtained is thoroughly washed, pressed, and digested in boiling alcohol, or in ether, to deprive it of oil, and then carefully dried. As it is thus procured, casein presents itself in white opaque masses (curds), resembling coagulated albumen, but much less firm. It is without odor or taste, is insoluble in water, alcohol, and ether, and when dried at a low temperature, presents itself in yellow horny-looking masses. It dissolves in weak solutions of the alkalies and their carbonates, and is thrown down from these solutions by acids: the precipitate is a compound of the acid and casein, and is soluble in an excess of the acid. Casein is also soluble in some saline solutions, as of common salt, sal-ammoniac, and nitre. Its compounds with the earths and metallic bases are insoluble in water: hence, milk may be beneficially used as an antidote in poisoning by many metallic salts. The casein of milk is precipitated by sulphate of copper. The caseate of oxide of copper is redissolved by potassa, forming a violet-blue solution: the oxide is not reduced to suboxide on boiling the liquid, unless sugar is present.

Casein is contained abundantly in peas, beans, and the seeds of leguminous plants; it is there associated with starch, and in the oily seeds, with albumen and emulsin. It may be obtained by digesting coarsely-powdered peas in cold or tepid water for two hours, allowing the starch and fibrous matter to subside, and then filtering the liquid. It forms a clear viscid solution, which is not coagulated by heat, unless albumen is also present; but like emulsin, and unlike albumen, it is precipitated by acetic acid. Casein is distinguished from albumen by its not coagulating when heated in a dilute solution, and by being precipitated from its solution by acetic acid. Like albumen, it is precipitated by tannic acid. The fact that it is coagulated by rennet (the lining membrane of the fourth stomach of the calf), as in the process of curd and cheese-making, it is also one of its distinctive characteristics. It contains sulphur, to the amount of 0·36 per cent. (MULDER), but no phosphorus—not at least in the peculiar state of combination in which that substance is found in albumen and fibrin; but it appears to be intimately combined with a certain proportion of phosphate of lime. The sulphur may be easily detected in it, by boiling the casein in a solution of oxide of lead in potassa. Like albumen and fibrin, casein is dissolved by strong hydrochloric acid at a boiling temperature, forming a reddish-purple-colored solution.

Casein is stated not to be coagulable by *heat:* but it is found in practice, that heat greatly facilitates the separation of the curd from milk when rennet or acids are employed. (*See* MILK, p. 651.) Thus, in procuring curd by rennet for the manufacture of *cheese*, the milk is heated to a temperature of 77° to 86°, and at the same time agitated. The casein separates in a mass, with more or less oil, according to the richness of the milk. The curds are pressed into masses, salted, and allowed to undergo a species of fermentation, by which their peculiar flavors are brought out. A rich cheese abounds in oil, a poor cheese in casein. The casein is generally colored of a pale-yellow to an orange-red color by annotto (*see* p. 625).

The method of obtaining cream in Devonshire and Cornwall, furnishes another proof of the influence of heat in aiding the separation of casein. After the cream has risen to the surface, in a pan of milk, instead of removing this by skimming or otherwise disturbing it, the pan is carefully heated over a charcoal fire, until bubbles of vapor begin to appear in the liquid, below the surface. A semi-solid mass is thus produced, consisting of the cream, with a very large proportion of casein. The milk which remains, is of course proportionably impoverished. (*See* MILK, p. 651.)

LEGUMIN is the name specially applied to the azotized caseous principle of peas, beans, and many similar seeds; it is considered as identical with casein by Liebig and Wöhler (LIEBIG, *Chim. Organ.*, iii. 220), and with emulsin by Dumas and Cahours (*Ann. Ch. et Ph.* 1842). A solution of it may be obtained from ground peas by the process above described (p. 637). Acetic acid diluted with 8 or 10 parts of water, is carefully dropped into the filtered solution and the legumin is precipitated: an excess of the acid should be avoided, as this would dissolve the precipitate. It falls in the form of white flakes, and after having been washed on a filter, it should be dried, pulverized, and freed from adhering fat, by digestion in ether. Legumin may be obtained from lentils with the same facility as from peas; but it is less easily procured from beans (haricots), in consequence of their containing a gummy matter, which interferes with its precipitation, and with the filtration of the liquids. The chemical properties of legumin are identical with those of casein.

Liebig supposes that grape-juice, and other vegetable juices which are deficient in albumen, derive their fermentative power from soluble legumin. This principle is soluble in tartaric acid, and to its presence he ascribes the tendency of sugar to form alcohol and carbonic acid, instead of mucilage and lactic acid.

GLUTEN.

Vegetable fibrin.—The term *gluten* is applied to the opaque, white, tenacious, and somewhat elastic substance which is obtained by subjecting wheaten flour to the continuous action of a current of water. The best mode of proceeding is to tie up the flour in a coarse cloth, and knead it under a stream of water until the starch and soluble matters are entirely washed out, and the water runs off clear. The residuary gluten should give no blue color with iodine water. According to some chemists, it consists of three distinct substances, of which *Vegetable fibrin* forms the largest proportion. *Gluten,* as it is thus extracted, is a white tenacious substance, capable of being drawn into long fibres. When dry, it becomes hard, horny and brittle, so that it is easily pulverizable. Macaroni is nearly pure gluten in a dry state, but generally associated with a little starch. Gluten when pure, undergoes no change of color on the addition of iodine. It is quite insoluble in water, but is dissolved by acetic acid, and a strong solution of potassa. It is again precipitated, when the acid and alkaline liquids are exactly neutralized. It contains sulphur, and is blackened when boiled in a potassa-solution of oxide of lead. It acquires a dark-red color when boiled in strong hydrochloric acid. Bread and macaroni, which chiefly owe their nutritious qualities to gluten, undergo similar changes. In a partially decomposed state, it forms *yeast,* and induces alcoholic fermentation in saccharine liquids. In all these characters it bears a close resemblance to fibrin.

The tenacious properties of dough, or the paste of flour, are mainly owing to *gluten.* It is more abundant in wheat and in rye than in other cereals; and in these grains, the gluten has a greater tenacity than in others: hence, they are better fitted for making bread. Calculated in the dry state, gluten forms from 7 to 14 per cent. of wheat flour, that of Odessa containing the largest proportion (Dumas). Gluten, as it is thus extracted from wheat flour, does not appear to be a pure vegetable principle. It contains cellulose and fatty matter: the latter may be removed from it by boiling alcohol or ether. It has been also supposed to contain another principle, analogous to albumen, called *Glutin:* but all chemical analogy is destroyed in the process by which it is extracted: If gluten is digested first in concentrated and afterwards in weak alcohol, in which albumen is quite insoluble, a yellow-colored liquid is obtained, which deposits a substance said to resemble casein, called vegetable casein. When the alcoholic liquid is poured off and evaporated, a yellowish viscid extract is obtained, to which the name of *glutin* has been given. It may be precipitated as a white substance by the addition of water to the alcoholic liquid. It still contains the oily matters which existed in the original gluten. In this process the greater part of the gluten remains unaffected by the alcohol, and this insoluble residue is called *Vegetable fibrin.* It is this substance which has the chemical properties of animal fibrin, that gives to the dough or paste of wheat flour, the peculiar tenacity which allows it to be converted into wholesome bread. Dumas and Cahours have proved by their analysis, that the undissolved gluten has the same chemical composition as dissolved glutin, the latter is, therefore, probably only a small portion of altered gluten removed by alcohol. Gluten is exclusively a vegetable product. Its general chemical characters have been but imperfectly ascertained.

FIBRIN.

Under this name a principle has been described common to animals and vegetables. Animal fibrin is obtained by agitating blood, as it flows from the vessels, with a rod, to the twigs of which it adheres in the form of fibrous filaments, which may be cleansed of coloring and other soluble matters by repeated washings in fresh portions of water. The essential character of this principle, as it is contained in blood, is its power of spontaneous coagulation. From a fluid state in this liquid, when removed from the living vessels, it speedily passes into a solid and insoluble condition, assuming a fibrous or reticulated form.

In its humid state, fibrin retains about 75 per cent. of water: it may be purified by digestion in ether, by which fatty matter is removed, and when dried at 240°, it is yellowish-gray, translucent, and horny. It is insoluble in water, but when long boiled, traces of ammonia are evolved, and a liquid is obtained which, when evaporated, leaves a substance having the smell of boiled meat: it does not gelatinize, but is precipitated by infusion of galls. The insoluble portion resembles coagulated albumen.

When fresh fibrin is covered with water, it becomes in a few days viscid, and acquires the odor of old cheese: it produces ammoniacal salts, and then the mixture gradually liquefies: in this state it is coagulated by heat, by the addition of alcohol, or of solution of corrosive sublimate, resembling in these respects, serum. Immersed in sulphuric acid, diluted with five or six parts of water, it shrinks, and a compound of the acid with fibrin is formed.

When fibrin is digested in nitric acid, nitrogen is evolved, and a yellow substance is produced, which has been termed *Xanthoproteic acid* (MULDER). Hydrochloric acid at first gelatinizes fibrin, and afterwards forms with it a blue liquid, which, on dilution with water, lets fall a white hydrochlorate of fibrin. When fibrin is immersed for about 12 hours in water, slightly acidulated by hydrochloric acid, it becomes gelatinous, and when this jelly is triturated with water, it yields a solution which coagulates by heat, is precipitated by ferrocyanide of potassium, and affords a precipitate on the addition of hydrochloric acid, not soluble except in an excess of this acid. These facts have some bearing upon the theory of digestion. According to Dumas and Cahours, water containing a millionth part of hydrochloric or hydrobromic acid, gelatinizes fibrin, and if a few drops of gastric juice (*pepsin*) be then added, it is entirely dissolved in a couple of hours at a temperature of 96° to 100° (*see* p. 655). Rennet produced the same effect.

Phosphoric acid with 1 atom of water acts upon fibrin in the same way as sulphuric acid. The acid with 3 atoms of water, converts fibrin into a gelatinous mass, which is soluble in water, and the solution is not affected by an excess of the acid. Fibrin is rapidly penetrated by concentrated acetic acid, and converted by it into a thick jelly soluble in hot water. When another acid (sulphuric) is added to this solution, a precipitate is formed composed of fibrin and the added acid. On the addition of an alkali (potassa) the fibrin is at first precipitated, but it is redissolved by an excess of the alkali. The fibrin of young animals is more easily acted on by acetic acid than that of old ones, so that there is in this respect a material difference between the fibrin of veal and of beef. (DUMAS.)

Fibrin is soluble in weak solutions of potassa and soda, first becoming gelatinous, and then forming a yellowish liquid which blackens silver and oxide of lead, and exhales the odor of sulphuretted hydrogen, on the addition of an acid. Caustic ammonia seems to act upon fibrin in the same way as the fixed alkalies, but its solvent action is less energetic. The fibrin of blood as it issues from the living body, *i. e.*, before it has coagulated, is soluble in from 6 to 8 parts of fresh serum, and also in a saturated solution of sulphate of soda. All liquids which dissolve this principle, prevent the coagulation of the blood (p. 649).

Ferrocyanic and ferricyanic acids combine with fibrin; the compounds are obtained in the form of white and yellow precipitates, by adding solutions of ferrocyanide and ferricyanide of potassium to the acetic solution of fibrin. The white precipitate is insoluble in the dilute acids, but the alkalies decompose it, and forming ferrocyanides, separate the fibrin in a gelatinous form.

The yellow precipitate (obtained by the ferricyanide) is more soluble than the preceding.

An alkaline solution of fibrin yields precipitates with several of the metallic salts—*e. g.*, sulphates of iron and copper, and corrosive sublimate. They are compounds of the respective oxides with the organic principle, which, owing to this combination, loses all tendency to undergo putrefaction. Tannic acid precipitates fibrin from its solutions, and the compound (tannate of fibrin) is imputrescible.

GELATIN.

This principle is abundantly diffused in the animal kingdom. It derives its name from the fact that a hot solution of it on cooling, sets into a jelly. A principle similar to it in gelatinizing properties, is found among vegetables, especially in certain kinds of algæ and fuci. Vegetable gelatin (*gelose*), which has already been described (p. 525) is, however, eminently distinguished from that of the animal kingdom, by the absence of nitrogen, and by a difference in its chemical properties. Animal gelatin is not included among the proteinaceous principles. When dissolved in potassa, no protein-compound is precipitated from the solution, on the addition of acetic acid. In constitution, also, it differs from the other principles considered in this chapter. When freed from all impurities, it contains no sulphur. Owing to these marked distinctions, it has been theoretically supposed to be deficient in nutritive power, and to have no claim to be regarded as a flesh-forming principle. There are no facts, however, to support this theory; on the contrary, experience shows that gelatin may be a source of nutriment to animals, although in a less degree than the fibrin and albumen (p. 645).

Gelatin is characterized by its insolubility in cold and solubility in hot water. It has been supposed that this principle had no independent existence in the animal body; but it is found abundantly in all young animals, in a state quite distinct from albumen, casein, and fibrin, which cannot be converted into gelatin by boiling water. It constitutes exclusively the middle portion of the air-bladder of the sturgeon and other fish, requiring only water for its solution; and it exists ready formed in skin, in a condition to produce tanno-gelatin, or leather, by simple immersion in a solution of tannic acid. Cold acetic acid will also dissolve gelatin from skin. There is, therefore, no ground for the statement that it is generated by the action of boiling water upon the membraneous tissues. In some instances, owing probably to its molecular condition, it requires a long application of heat for its perfect extraction by water; but in all cases, it must be regarded as an *educt* and not as a product.

The term *gelatin* was long indiscriminately applied to all the gelatinous substances, obtained by the action of boiling water on bone, cartilage, and ligament, until Müller pointed out the peculiarities of the product derived from *cartilage*, and appropriated to it the name of *Chondrin.* (*Poggend. Ann.*, xxxviii. 305.)

To obtain common *gelatin*, the substances affording it, such as the clippings of hides, hoofs, horns, calves' feet, cows' heels, sheep's trotters, are cleansed in cold water, and then subjected to the action of boiling water. The solution so obtained, is freed from fat, and from any deposit, by skimming and straining, and allowed to gelatinize on cooling: the jelly so formed is more or less colored and impure. It is cut into slices and dried.

Fish Gelatin.—*Isinglass* (probably a corruption of *hasenblase*, bladder of the sturgeon). This is a variety of commercial gelatin which is largely consumed as an article of food, and is chiefly prepared in Russia from the air-bladders and sounds of certain species of *Acipenser*, or sturgeon. The bladders are cleansed, dried, and scraped so as to separate from them, the external and internal membranes; and without further preparation, the residue forms *leaf isinglass.* Isinglass was formerly picked into shreds, but is now usually cut into delicate filaments by machinery. It should be colorless, inodorous, and tasteless; soluble in hot water after a short maceration in cold water: and when incinerated, it should leave only traces of phosphate of soda and of lime. There are many varieties of isinglass. The Beluga leaf, from Astrachan, is the best, while the Brazilian isinglass is of the worst quality. All kinds of commercial isinglass contain a certain amount of insoluble albuminoid matter, which is precipitated on cooling the hot solution. We have found this to amount to 2 per cent. in the best quality, and to as much as 20 per cent. in the worst. When any of the varieties of isinglass are refined, they yield the pure principle gelatin, which is identical with that obtained from the fresh skins of calves and bullocks by the process mentioned below.

Skin Gelatin.—A very pure form of gelatin sold under the name of *Patent Refined Isinglass* is manufactured from glue-pieces, or the cuttings of the skins of calves and bullocks. These are cleansed of fat and dirt by washing in lime-water: they are then sliced and digested in water, at a temperature of about 200°. The gelatinous liquid strained through flannel, is allowed to cool until it has acquired a proper consistency. It is then poured on a slab of wet slate, and when nearly set, the sheet of gelatine is transferred to an open network for the purpose of drying. It is subsequently damped, rolled into thin sheets, and cut by a machine into fibres of various degrees of thickness. This process applied to Brazilian and other impure kinds of commercial isinglass, yields equally pure gelatin. A cheaper form of gelatin, but improper as an article of food, has been manufactured, under a patent, by digesting glue-pieces in an alkaline liquid, and afterwards boiling down the whole of the tissues.

Bone Gelatin.—This is obtained by heating ground or rasped bones with water, under pressure, to a temperature of 250° to 270°; the liquor gelatinizes on cooling, and the jelly may be purified as in the previous cases. But the gelatin thus procured, always retains an offensive odor when moist and a disagreeable flavor, in consequence of the high temperature employed. Another mode of obtaining bone jelly consists in digesting the bones, previously boiled in water to remove the fat, in dilute hydrochloric acid, so as to abstract the phosphate of lime. The animal part of the bone is thus left, having the appearance of a tough flexible cartilage: this is thoroughly washed in water, steeped in lime-water, or in a weak solution of carbonate of soda, and again washed and dried. The dried bone gelatin may then be made into glue or size by boiling, gelatinizing, and drying, as with the other forms of gelatin. It has been sold as an article of food in thin sheets, and sometimes colored to conceal its impurity, under the name of French gelatin. It is a variety of glue.

From whatever source obtained, *pure gelatin* is colorless, transparent, inodorous, and insipid: it may have no smell in the dry state, and therefore it should be tested by immersing a small quantity in boiling water. The agglutinated mass, if a bad sample, will have the offensive odor of glue. The fibre of pure gelatin is translucent, and when wetted, more or less elastic, tough, and resisting. It at the same time nearly retains its transparency. The fibre of isinglass, in which gelatin is always associated with albuminoid matter, becomes quite opaque when wetted, is inelastic, and without cohesion. Gelatin is heavier than water. When heated it softens, then shrinks, and exhales a peculiar odor, burning with difficulty, and exhaling the ammoniacal odor of burned horn or feathers. Subjected to destructive distillation, it yields an abundance of carbonate of ammonia, together with the other products of azotized organic matters, and leaves a bulky carbon difficult of incineration.

In cold water gelatin gradually softens and swells, but scarcely dissolves until gently heated, and on again cooling the solution, it forms a more or less firm jelly. By its solubility in hot water it is distinguished and separated from fibrin and albumen. According to Bostock 1 part of isinglass dissolved in 100 of water, gelatinizes on cooling; but in 150 of water it remains liquid. We have found that 1 part to 80 of water, was required to produce a moderately firm jelly. This effect, as is well known, varies much with temperature, so that jellies are more easily prepared in winter than in summer. The stiffness of the jelly is also greatly dependent upon the source whence the gelatin was originally obtained; the skins and tissues of old animals yielding a stronger and firmer jelly than that derived from young animals. The gelatinous mass cannot be regarded as a definite hydrate. The water slowly evaporates or may be imbibed by porous substances, and the gelatin then remains in a dry state with its original properties. The gelatinous condition is common to organic and mineral matter. Silica and alumina may be obtained in a gelatinous state (p. 284).

When a solution of gelatin is repeatedly warmed and cooled, especially if boiled, it gradually loses its tendency to gelatinize, and it becomes more and more soluble in cold water. In close vessels, jelly may be kept in cool weather for some days without change; but in open vessels, it soons becomes mouldy. It then putrefies and exhales a disagreeable ammoniacal odor. A little acetic acid considerably retards these changes without materially affecting gelatinization. The fresh-made aqueous solution is neutral, and should have no smell or taste. A solution of isinglass commonly has a slight fishy odor and taste.

Gelatin is not soluble in absolute alcohol; and when alcohol is added to a warm and strong aqueous solution, the gelatin separates in the form of a white viscid substance. It is insoluble in ether, and in fixed and volatile oils.

Gelatin is soluble in all the dilute acids, excepting the tannic, differing essentially in this respect from albumen; of these, the acetic solution only, gelatinizes on evaporation. Gallic acid gives no precipitate with it. When the dilute nitric solution of gelatin is evaporated, nitrous gas is evolved, and the residue deflagrates just before dryness; with strong nitric acid, oxalic acid is formed. The action of the strong sulphuric acid on gelatin is attended by the formation of *leucine*, and of a peculiar saccharine product, which is known under the names of *glycocol* or *glycocine*. It is gelatin-sugar (p. 644).

The dilute caustic alkalies, and ammonia, do not prevent the gelatinization of gelatin, but they often throw down a portion of phosphate of lime. When gelatin is dissolved in a dilute solution of caustic potassa, and exactly neutralized by acetic acid, the evaporated liquid does not gelatinize on cooling. When boiled with caustic potassa, ammonia is evolved, and leucine and gelatin-sugar are formed. Acetic and nitric acids produce no precipitate in an aqueous solution of gelatin. The addition of common salt or other neutral salts, or of ferrocyanide of potassium, to the acetic solution, does not cause the precipitation of gelatin. When gelatin is dissolved in a weak solution of potassa, acetic acid does not affect the liquid. When a solution of chloride of lime is added to gelatin in acetic acid, a turbidness is produced.

A solution of gelatin is not precipitated either by the neutral acetate, or by subacetate of lead. With protochloride of tin it gives a flocculent precipitate, but none with the perchloride. With sulphate of copper there is no precipitate. When a solution of gelatin is gradually added to one of corrosive sublimate, a cloud is formed which at first disappears, but afterwards a coherent elastic substance is thrown down. The nitrates of mercury produce the same effect. Gelatin is not precipitated by solution of silver or of gold, but sulphate of platinum throws it down in brown viscid flakes, which blacken and become brittle when dried on a filter. E. Davy recommends this as a delicate test for gelatin, detecting it in solutions too weak to be affected by tannic acid, and not liable to be interfered with by the presence of albumen. (*Phil. Trans.*, 1820, p. 119.) Neither sulphate of alumina nor alum occasions any precipitate in a solution of gelatin; but a mixture of chloride of sodium and alum, or a solution of chloride of aluminum, form a white precipitate: this compound exists in *tawed leather.*

Tannic acid is a most delicate test of the presence of gelatin; when it is added to a solution of 1 part of gelatin in 5000 of water a cloud is evident, and on dropping tincture or fresh infusion of galls into a strong solution of gelatin, a dense white curdy precipitate of tanno-gelatin falls, which becomes gray when dried, is insoluble in water, and not putrescible. Mulder has described two definite combinations of tannic acid with gelatin: 1, one containing 1 atom of gelatin and 1 of tannic acid, which is thrown down when a great excess of the latter is used; and 2, one containing 3 atoms of gelatin and 2 of tannic acid, formed when the latter is not added in excess. According to Davy, when gelatin is precipitated by infusion of oak-bark, 100 parts of the precipitate contain 54 of gelatin and 46 of tannin. Schiebel found that when a solution of 100 parts of gelatin is precipitated by a great excess of an infusion of 1 part of oak-bark in 9 of water, it combines with 118 parts of tannin; but when a weak solution of extract of oak-bark is added to a solution of gelatin, so as not to precipitate the whole of the latter, the precipitate which slowly falls, contains 100 of gelatin and 60 of tannin. As albumen is also precipitated by tannic acid, when this acid is used as a test for gelatin, the absence of albumen should be previously ascertained. Tanno-gelatin is identical with *leather.* In the manufacture of leather, the precipitate is formed in the skin itself, by immersing it first in a weak and afterwards in a strong infusion of oak-bark. The albumen of the skin is also at the same time converted into tannate of albumen.

A solution of fish-gelatin (isinglass) has the same properties as that of skin-gelatin; the latter is not so rapidly dissolved by hot water, but it dissolves entirely, leaving no sediment, like isinglass. A solution of bone-gelatin differs from both of these in the fact that as phosphate of lime is soluble in gelatin, oxalate of ammonia produces a turbidness in its solution. As isinglass is frequently adulterated with bone-gelatin, oxalate of ammonia occasionally produces a turbidness in its aqueous solution.

Leucine ($C_{12}H_{12}O_4N$) so called from its white appearance. This compound, which bears some resemblance to cholesterine, may be procured by boiling gelatin in sulphuric acid, diluted with 4 parts of water. It is also obtained with *tyrosine,* when dry casein is fused with its weight of hydrate of potassa. *Tyrosine* ($C_{18}H_{11}O_6N$) may be precipitated from the lixivium by the addition of acetic acid. Leucine melts at 350°, and undergoes decomposition. This substance is also known under the names of *Caseous oxide* and *Aposepedine.* It may be obtained from the fibrin of muscle, from gluten, and other nitrogenous principles.

Glycocine ($C_4H_5O_4N$), *Glycocol. Gelatin-sugar.*—This is another product of the reaction of dilute sulphuric acid on gelatin at a boiling temperature. It is also procured as a result of the action of hydrochloric acid, at a boiling temperature, on one of the organic acids of bile, or on hippuric acid. It assumes a crystalline form, is not very soluble in water, and is insoluble in alcohol and ether. It has a sweet taste, but differs from sugar in not undergoing vinous fermentation. When treated with nitric acid, no oxalic acid is formed; but a new acid, called the *Nitro-saccharic*, is produced. The interest attached to this product, lies in the variety of sources from which it may be obtained, and in the numerous compounds which are derived from it.

The three nitrogenous principles, *albumen, fibrin*, and *casein*, are the constituents of animal food; and the fact that principles of a precisely similar nature are found in the vegetable kingdom, shows that, chemically speaking, there is not that broad distinction between animal and vegetable food which some have imagined. The constituents of flesh, *i. e.* fibrin and albumen, exist in vegetables, and from these vegetable principles, the flesh of herbivora must be formed. These two principles find their way directly into the blood through the medium of the chyle, the liquid product of digested food. *Gelatin* is not found in the blood, but it is no doubt formed from it in the living body. With reference to the human body, it can be properly nourished only by a variety of food, to suit the variety of textures of which it is constituted. A theory was formerly propounded to the effect, that the body could be supported by any one of these nitrogenous principles, excepting gelatin; but a Commission of the French Academy reported, upon due inquiry, that this observation was equally applicable "to albumen, fibrin, or casein, if employed alone; and that neither animals nor man should be restricted to any course of diet which does not contain *all* the proximate principles of the frame." (TODD and BOWMAN). These four principles, under the influence of life, appear to be convertible into each other. This is proved to some extent by the process of incubation. The recently laid egg contains only soluble albumen and oil. When incubation is complete, fibrin and gelatin are found in the muscles and soft parts of the young bird, and a large proportion of the soluble albumen has passed into the insoluble state (p. 634). Casein, as it is contained in milk, is necessarily converted in the living body into the other principles (*see* p. 634).

Various formulæ have been assigned to gelatin. That which is now generally admitted, represents its constitution as $C_{13}H_{10}O_5N_2$. It contains a large proportion of nitrogen, but no sulphur. When pure gelatin is dissolved by boiling it in a solution of potassa, containing oxide of lead, no discoloration is produced. The contrary statement appears to have arisen from the application of this test to commercial isinglass, which always contains a certain proportion of albuminoid tissues. When these have been separated by refining the isinglass, the resulting gelatin produces no effect in a potassa-solution of oxide of lead.

Size is usually sold in the form of a stiff tremulous jelly: it is obtained chiefly from the waste of vellum, parchment, and from the skins of horses, cats, dogs, and rabbits, and sometimes from fish. It is largely employed in the manufacture of paper, and by whitewashers, painters in distemper, paper-stainers, and gilders. Size has usually a putrid odor and taste, and a brown color.

Glue is an important article of manufacture, and differs in price and quality according to its source. It is extracted from bones, muscles, tendons, ligaments, membranes, and skins, the latter yielding the best glue, especially when from old animals. The parings of hides and pelts from tanners and furriers, the hoofs and ears of horses, oxen, calves, sheep, &c., are employed in the manufacture of glue. They are first digested in lime-water, washed, laid in a heap to drain, and boiled in soft water; the impurities are carefully skimmed off, and the liquid is then strained, clarified with a little alum, and allowed to settle. The solution is poured off from the sediment, and boiled down to a proper consistence, so as to concrete on cooling: the glue is then cut by a wire into slices, which are dried upon netting. Good glue is hard, brittle, of a uniform brown translucency, and when immersed for some time in cold water, it becomes soft and gelatinous, but requires to be heated, in order to dissolve and fit it for use. It should be heated over a gentle fire, or in a water-bath, and it may then be applied to the moistened wood by a stiff brush: it will not harden in a freezing temperature; the adhesion depends upon the absorption and evaporation of the superfluous water.

Chondrin.—This variety of the gelatinous principle constitutes cartilage, as it exists in the windpipe, nose, and ear, as well as in the cornea of the eye, in the ribs, and at the ends of the long bones. It is found abundantly in the flesh and cartilaginous skeletons of fish, and from fish-bones; it may be readily extracted by boiling water. If sufficiently concentrated, the solution sets into an opaque jelly on cooling. It is not so soluble in hot water as gelatin. An aqueous solution of chondrin is precipitated by acetic acid, but the precipitate is dissolved by an excess of the acid. It is precipitated by nitric and tannic acids, as well as by sulphate of copper and acetate of lead. It is not affected by caustic alkalies. Its formula is $C_{32}H_{26}O_{14}N_4$.

The nitrogenous principles which we have here considered, build up the animal body. The soft solids of animals are chiefly formed of fibrin, albumen, and gelatin.

Fibrin enters largely into the composition of muscle or flesh; thus, assuming that the proportion of water varies from 71 to 74 per cent., the fibrin in muscle, averages from 19 to 22 per cent., and the gelatin from 5 to 7 per cent. In addition to these constituents, muscle consists of cellular tissue, (albumen) nerves, vessels, and fat. Dry muscle yields, by ultimate analysis, the same elements as blood. In the juice of flesh, which is always acid, crystalline nitrogenous principles exist, which may be separated by complex processes. Among these may be enumerated *Kreatine* ($C_8H_9O_4N_3+2HO$) and *Kreatinine* ($C_8H_7O_2N_3$): this is also a product of the decomposition of kreatine. *Inosinic* or *Inosic acid* ($C_{10}H_6O_{10}N_2+HO$) and *Sarcosine* ($C_6H_7O_4N$) are other principles, the former being an educt of the juice of flesh, and the latter a product of the decomposition of kreatine. *Inosin* ($C_{12}H_{12}O_{12}+4HO$), a variety of sugar, has been found in the juice of the involuntary muscles. *Osmazome* (ὀσμὴ, *odor*, and ζωμὸς, *broth*) is not a definite compound, but an alcoholic extract of the residue left by a watery extract of flesh.

Albumen enters into the composition of muscle, of the brain, spinal cord, and nerves. It is a constituent of cellular tissue, and of the soft organs, such as the liver, spleen, lungs, and kidneys. The substance of the brain consists of 80 per cent. of water, with 7 per cent. of albumen in a soluble form. It contains two acids, a solid white fatty acid (the *cerebric*), and an oily liquid, the *oleophosphoric*, acid. The cerebric acid contains phosphorus. The waxy secretion of the ear (*Cerumen*) is a compound of albumen with an oily matter, and a yellow bitter extract, which is soluble in alcohol.

Gelatin enters into the composition of the skin, tendons, ligaments, and the white fibrous tissue generally, as well as of bone, cartilage, ivory, and the teeth of animals. 100 parts of dry human *bones* contain about 33·3 of organic matter (gelatinous tissue), and 66·6 of earthy matter, consisting chiefly of subphosphate of lime with carbonate of lime and phosphate of magnesia. Fluoride of calcium is found only in fossil bones. The proportions of organic and inorganic matter, vary slightly in the bones of different animals, and in the different bones of the same animal. The proportions of mineral and organic matter also vary at different periods of life. Thus, according to the analysis of Schreger, in the child, the earthy matter forms nearly one-half of the weight of the bone (48·48 per cent.): in the adult three-fifths (74·84 per cent.), and in old age seven-eighths (84·10 per cent.). The bones, at this period of life, contain much oily matter. The mode in which the organic and inorganic constituents are blended in the skeleton, is worthy of remark. When a fresh bone, *e. g.*, the scapula, is digested in dilute hydrochloric acid, all the mineral matter is removed (p. 642): but the bone perfectly retains its shape. The residue consists of flexible and elastic gelatinous tissue. If a similar bone is carefully heated to a high temperature, under a free access of air, a white brittle mineral substance is obtained, which retains the perfect shape of the bone. This consists of phosphate and carbonate of lime. These results show that every atom of mineral is associated with an atom of organic matter. Bones contain, not merely in their hollow interior (*cancelli*), but in their substance, a large quantity of oily matter which is profitably extracted by simply boiling crushed bones in large caldrons of water. It rises to the surface like an oil, and is removed in a solid cake when the liquid has cooled. Bone fat, or grease, is now manufactured weekly by tons in this metropolis. Its composition does not differ from that of other animal fats, and it contains the same principles, but rather a large proportion of oleine (p. 576). Bone fat is soft, inodorous, and easily fusible. It is largely used in the manufacture of pomatum, "bear's grease," and other cosmetics, and is employed for some of the finer kinds of toilet soaps, in preference to other animal fats. When bones are heated in close vessels, they leave a porous charcoal, which is usefully employed in chemistry and the arts, under the name of animal charcoal (p. 243).

Ivory has a composition similar to that of bone. The dentine or bony part of the teeth, contains from 68 to 70 per cent. of mineral matter; while the enamel contains 84 per cent. with 6 per cent. of gelatin. *Pearls* and mother-of-pearl contain 66 per cent. of carbonate of lime and 34 of organic matter. *Shell*, coral, and madrepore are chiefly composed of carbonate of lime cemented with animal matter. The shell of the egg contains 98 per cent. of carbonate of lime, and 2 per cent. of organic matter. The effect of incubation is to render it thin and brittle.

In the shell of the lobster and crab, the mineral matter appears to be cemented by another organic principle, *Chitin* ($C_{17}H_{14}O_{11}N$). It is insoluble in water, but soluble in strong acids. It enters into the composition of the elytra of certain insects, *e. g.*, the cockchafer, cockroach, and beetles.

CHAPTER LVI.

THE FLUID CONSTITUENTS OF ANIMAL BODIES, AND THE SUBSTANCES DERIVED FROM THEM.

Although water is commonly regarded as a compound belonging to the inorganic kingdom, it is a most abundant, and certainly a most important, constituent of animal bodies. At least two-thirds of the weight of the human body, are represented by water. If we except the bones, this liquid forms three-fifths of the solid organs and textures, and about four-fifths of the fluid constituents. The flexibility, softness, elasticity, and tenacity of the tissues are due to the presence of water. Fibrin and albumen, when deprived of it, lose their most important physical properties as parts of a living structure; and it is a matter of demonstration, that without it, vital action cannot continue. At p. 504 we have given the results of recent analyses, whereby it is proved that some vegetables contain 96 per cent. of this liquid; and at p. 130 we have referred to the constitution of the *Acalephæ*, animals which contain 99 per cent., and which might almost be described as living water. From calculations based upon the analysis of bone, and of the solid and fluid constituents of the human body, we find that the body of a male adult, weighing 150 pounds, consists of water 100 pounds; dry organic solids 34 pounds; earthy or *mineral matter*, chiefly the phosphate and carbonate of lime and chloride of sodium, mixed with small quantities of other earthy and alkaline salts, and oxide of iron, 9 pounds; and of oil, or fat, 7 pounds. The amount of mineral matter has been deduced from the actual weighing of dry adult skeletons; and the fat from the calculations of Burdach, who estimates it at about 5 per cent. of the weight of the body. The ordinary analyses of the solid and fluid constituents, furnish the remaining elements of this calculation. It is probable that the proportion of water is even greater than that which is here assigned; as it is, it amounts in an adult to 100 pounds or ten gallons! If we carry this inquiry into the proportions of the *elements*, as they are known to constitute the dry organic solids, and the oil or fat, we arrive at the following results: Of the 41 pounds of the dry solids and of oil or fat, carbon forms 23 pounds; oxygen 8 pounds; nitrogen 6 pounds; hydrogen 3½ pounds; and sulphur and phosphorus together (the former preponderating), half a pound. This is exclusive of the oxygen, hydrogen, carbon, and phosphorus, which exist in the water and mineral matter.

The fluids of the animal body may be divided, according to their principal chemical characters, into, 1. Those which are at the same time fibrinous and albuminous; 2. Those which are albuminous; and 3. Those which are non-albuminous. Gelatin is not found in any of the fluids: it exists in the body only as a component of the solid tissues. All the fluids in a healthy state contain albumen, excepting the bile and urine. In certain diseased states of the body, albumen is found in the last mentioned liquid. Casein exists chiefly in the milk, a secretion peculiar to the class mammalia. The *fibrinous* and *albuminous liquids* are the blood, chyle, and lymph.

1. The Blood.—In mammiferous animals, the blood is of a red color; florid and approaching to scarlet in the arteries, and of a deep purple in the veins. Its sp. gr. varies between 1·049 and 1·057, and its temperature in the healthy human body is between 98° and 100°. It has an unctuous or somewhat soapy feel, a slightly nauseous odor and saline taste, and an alkaline reaction. It appears homogeneous, or uniform, whilst circulating in its vessels, or immediately upon its removal from them; but when examined by a microscope, it is seen to consist of numerous red particles or cells, varying from one-three thousandth to one-six thousandth of an inch in diameter, floating in a colorless transparent fluid; the former having been termed the *red corpuscles*, the latter the *liquor sanguinis*.

The corpuscles of blood are mechanically diffused in the serum, in which the fibrin is dissolved. Under ordinary circumstances, the blood, after it has been drawn from its vessels, gelatinizes, or coagulates; and the jelly, or coagulum, gradually separates into two parts, a liquid serum, and a soft clot or *crassamentum*. In the act of coagulation, the corpuscles apparently coalesce and give to the clot a uniformly red color. This arises from the tendency of fibrin, when removed from a living bloodvessel, to assume the solid and insoluble state. The particles of fibrin cohere in a sort of fibrous network, retaining the red corpuscles in the interstices. The proportion which the clot bears to the serum is variable, and is partly dependent upon the shape of the vessel in which the blood is contained. According to Lecanu, in 1000 parts of healthy blood, there are 869 parts of serum and 131 of clot, which he describes under the general name of "globules." The mode of procuring fibrin and its chemical properties have been already described (p. 640). The corpuscles consist of an envelope or membrane holding a liquid of an albuminoid nature (*globulin*, p. 636), deeply tinged by a very small proportion of an organic coloring-matter (*hæmatosine*, $C_{44}H_{22}N_3O_6Fe$). The proportion of fibrin in recent healthy blood, is from 2 to 3 parts in 1000 by weight, and the proportion of coloring principle (*hæmatosine*) is rather less than this. The clot (or globules of Lecanu) may therefore be considered to be thus constituted in 1000 parts of blood:—

Fibrin	2·948
Hæmatosine (coloring matter)	2·270
Globulin (albumen)	125·627
	130·845

Arterial blood has not been found to contain more fibrin than venous blood, but capillary blood contains less than either. With the exception of color, there is no marked physical or chemical difference between arterial and venous blood.

Hæmatosine. Coloring-matter.—This consists of small corpuscles, bladders, or flattened cells, containing a red coloring principle combined with globulin. It is to their great number and aggregation, that the blood owes its red color. In the mammalia, they are not spherical, hence the term globule is inappropriate. They are disks of the shape of a circular double concave lens, being thicker at the circumference than in the centre. In the Camel tribe, they are of an oval form, but, in these, as in other mammalia, there is no nucleus. In birds, reptiles, and fishes, they are of an oval shape, and have a nucleus in the centre. Their size bears no proportion to the size of the animal. They have the same size and form in the human being at all stages of growth; but the average size varies in different animals. They are larger in man than in most domestic animals, while they are smaller in the sheep and goat, than in the pig, hare, and rabbit. In man, they have an average diameter of 1-3200 of an inch: in the goat of 1-6366th of an inch.

Müller found that these particles were so large in the blood of a frog (1-2745th of an inch), that they might be separated by filtration. The liquor sanguinis passed through the filter, and the fibrin separated spontaneously from the albumen, in a colorless state.

In the blood, there are also colorless nucleated corpuscles of a spherical form which are rather larger than the red corpuscles. They are similar to the nucleated particles found in lymph and chyle.

The red corpuscles in human blood have a sp. gr. of 1·0885, and as the sp. gr. of serum, in which they are diffused, is 1·030, they have a tendency to sink in this liquid. The corpuscles may thus be collected and examined in serum, which does not dissolve the coloring-matter, as it is contained in them. The *coloring-matter* is an organic principle containing nitrogen and iron in some unknown state of combination. It has an intense coloring power; and on the breaking of the outer membrane of the corpuscles, the red color is diffused and communicated to water or other liquids. The proportion of iron has not been accurately determined, but it is supposed to form from 0·43 to 0·5 per cent. of the dried corpuscles, or 6 per cent. of the pure coloring-matter. The albuminous principle, globulin, is dissolved by water, hence an aqueous solution of the coloring-matter, always contains a portion. It may be separated by a mixture of alcohol and sulphuric acid, by which globulin is coagulated, while the coloring-matter, as it is supposed, is unaffected.

An aqueous solution of the coloring-matter, when recent, has an intensely red color, and a peculiar odor: it is quite neutral. When the solution is heated to about 150°, the hæmatosine is coagulated and destroyed, the liquid assuming a muddy brown color. It is now rendered quite insoluble in water. Nitric acid and chlorine destroy the red color, turning the liquid brown and greenish brown. Weak alkalies (ammonia) in small quantity, have no effect upon the color. In excess they darken it. Neutral salts produce no change in it. Alcohol and tannic acid render the solution turbid, but do not destroy the red color.

The *serum* of blood is a pale straw-colored albuminous liquid, of a slightly alkaline reaction. Its sp. gr. is 1·030: it contains about 90 per. cent. of water. It sets into a coagulum when heated to about 160°. Its properties have been already described under the head of seralbumen (p. 633).

The blood contains fatty and saline matters, the latter consisting chiefly of alkaline chlorides and phosphates. Its composition concisely stated would therefore stand thus, according to recent analysis (Regnault):—

ANALYSIS OF VENOUS BLOOD IN 100 PARTS.

Clot or crassamentum	13·0
Serum	87·0
	100·0

Clot	Fibrin		0·30
	Globules	Hæmatosine	0·20
		Globulin	12·50
			13·00
Serum	Water		79·00
	Albumen		7·00
	Oily or fatty matters		0·06
	Chloride of sodium and other salts		0·94
			100·00

The use of the blood is to maintain, by its incessant distribution to all parts of the body, the life of an animal. It has been described as "liquid flesh" (Bordeu): it contains the animal solids in a state of solution; and analysis shows that blood and flesh yield as nearly as possible, the same elements in the same proportions. The daily waste of the blood is supplied by the *chyle*. With the exception of chyle and lymph, all the fluids and solids of the body, are formed by the blood, and at the expense of its constituents. On the other hand, in the formation of the body of the young bird, during the process of incubation, blood, with its usual constituents, fibrin and hæmatosine, is actually produced from soluble albumen. That such widely different products as milk, bile, and urine, should be produced in the living body from the constituents of this fluid, with such remarkable uniformity and regularity, is one of those marvels of vital chemistry which science cannot explain.

Tests for Blood.—Blood-stains on articles of clothing may be identified —1. By their peculiar crimson-red color. 2. By the shining and raised surface of the stain or spot (dried albumen and fibrin). 3. By their ready solubility in water, to which they give a red color. The water under these circumstances contains albumen, as well as hæmatosine. Weak ammonia does not change the red color to a blue, green, or crimson tint. When boiled, the albumen and hæmatosine are both coagulated, and the red color is entirely destroyed; a muddy brown coagulum subsides, which is quite insoluble in water and alcohol. For the examination of small stains in a dry state, an inch power of the microscope will be found convenient.

By employing a small quantity of water on a glass slide in order to dissolve the stain, the clot may be broken up and the red corpuscles separated. These may be examined by a quarter-inch power under the microscope. When detected, the evidence of the presence of blood, is placed beyond doubt. No other red coloring matter, vegetable or animal, owes its color to corpuscles or cells. A small quantity of glycerine added to the water which is used as a solvent, prevents it from drying too rapidly.

[It would carry us far beyond the scope of this Work, if we entered into more minute details on the chemistry of the blood. No treatise on the science can supply the special information now required by students of medicine, on the physiological and pathological chemistry of this important fluid. We therefore advise the reader who desires further information, to consult one of those numerous monographs which have been published on the subject: and we recommend among others Dr. G. O. Rees' treatise on the "Analysis of the Blood and Urine." The remarks here made respecting the blood, apply with equal force to the pathological chemistry of the urine. Dr. Rees' book, or the late Dr. Golding Bird's work on "Urinary Deposits," may be profitably consulted for full information on those points, which are necessarily only briefly noticed in this chaper on the animal fluids.]

2. Chyle.—This is a milky-looking liquid which is found in the thoracic duct. It has an alkaline reaction. It appears to consist of oily matter, in a state of emulsion, with an albuminous liquid. Under the microscope, oil-globules and colorless nucleated globules (chyle-globules) are visible. A fibrinous clot, which amounts to from 1 to 6 per cent. of the liquid, separates by spontaneous coagulation, as in the blood, and no doubt owing to the same cause—*i. e.*, the natural tendency of this principle, when not in free motion in a living vessel, to assume a solid and insoluble state. An analysis made by Dr. Rees, shows that 100 parts of healthy chyle consist of 7·08 albumen, with traces of fibrin, extractive matters (undefined), 1·08; fatty matters, 0·92; chloride of sodium and other salts, 0·44; water, 90·48. The chyle conveys the elements of nutrition immediately into the blood by means of the thoracic duct.

3. Lymph.—The fibrin and albumen in this liquid, as it is circulated in the lymphatics, are generally stated not to exceed 1 per cent. In an analysis of lymph made some years since, we found the liquid, which was feebly alkaline, to consist of albumen and fibrin, 2; saline matters, 2; water, 96.

The *albuminous* liquids are very numerous, and comprehend all the *secretions* of the body, excepting bile. They are either alkaline or neutral, generally the former, and their principal saline ingredients, are chloride of sodium, carbonate of soda, and the phosphates of soda and lime. The most important of these liquids is the *milk*, which is secreted from the blood by the mammary glands, and is necessary to the nourishment of the young of the class mammalia.

4. The Milk.—This is an opaque white liquid consisting of water, casein with some albumen, sugar (lactine) with lactic acid, oil (butter), and salts. When examined by the microscope, it is found to contain oil-globules of various sizes, floating in a clear liquid (serum or whey). These globules are remarkable for their perfect sphericity in all respects, as well as for the brightness of their middle portions in contrast with the dark circumference, an optical effect depending probably on the refractive power of the oil,

which appears to be contained within a transparent membrane. The opacity of milk, is owing to the number and diffusion of these oil-globules, which vary in diameter from 1-900th to 1-2500th of an inch. They give to the liquid the character of an emulsion, like that produced when the pulp of the almond is mixed with water.

When milk is allowed to stand, it separates spontaneously into two portions. The oil-globules, by reason of their low specific gravity, collect upon the surface, forming *cream*. The richness of milk is determined by the relative thickness of this stratum, and for this purpose the milk is placed in a graduated tube called a *lactometer*.

The oil-globules are not dissolved by ether, on simple agitation with milk, until a little acetic acid has been added, and the liquid boiled. In this case the membranes are dissolved by the acid, and the oily portion, as it is set free, by the ether. Butter is the result of the aggregation of the oil-globules. The separation of the oil in this form, is commonly effected by the process of churning, which consists in the mechanical agitation of the cream at a moderate temperature. The milk of all animals is, in its normal state, neutral; although it very soon exhibits acidity when exposed to air, in consequence of the formation of lactic acid. This, after a time, causes the separation of casein in the form of coagulum. The sp. gr. of milk varies; that of the cow is generally about 1·030. It fluctuates in different animals, according to Brisson, from 1·0203 to 1·0409; but as it is affected by the presence of the butter on the one hand, which diminishes, and by the casein and salts on the other, which increase its density, it is difficult to estimate a mean. According to Berzelius, the sp. gr. of skimmed milk, is 1·033; that of cream 1·024.

Some of the principal properties of milk are due to the presence of *casein*, the chemical peculiarities of which have already been described (p. 637). Fresh milk does not coagulate when boiled. A firm and coherent pellicle forms upon the surface when it is boiled in air, as the result of the oxidation of a part of the casein; and on the removal of this, a fresh pellicle is formed; but there is no coagulum. In this form, casein is insoluble in water. By direct analysis, we found that 100 parts of good cow's milk yielded of water 86·4, organic matter 12·6, and saline matters 1. The proportions of oil, casein, and sugar are subject to great variation in different animals, as well as in the same animal, according to its state of health and the substances on which it feeds. The milk is sometimes a source of elimination of noxious substances which may have been taken in the food. According to Regnault, the following represents the constitution of 100 parts of this liquid in various animals:—

	Cow.	Ass.	Goat.	Mare.	Bitch.	Human Fem.
Water	87·4	90·5	82·0	89·6	66·3	88·6
Oil or butter	4·0	1·4	4·5	traces.	14·0	2·6
Lactine and soluble salts	5·0	6·4	4·5	8·7	2·9	4·9
Casein, albumen, and fixed salts	3·6	1·7	9·0	1·7	16·8	3·9
	100·0	100·0	100·0	100·0	100·0	100·0

The salts of the milk, are here chiefly included in the weight of the casein and albumen. They amount to only 0·37 per cent., of which 0·18 are phosphate of lime, and 0·135 chloride of sodium. The phosphates of magnesia, soda, and iron, are found in traces, as well as carbonate of soda. It is stated by some authorities that casein contains no phosphorus; but it is certain that phosphates are rather abundantly obtained in the ash.

The *colostrum*, or milk as it is first secreted, is thicker than milk, and of a yellowish color. Under the microscope, it presents oil-globules, mucus, and granules of an irregular shape. It contains 17 per cent. of solid matters, including casein. The analysis of cream, shows that it consists of about equal parts of butter and casein, with a variable quantity of serum or whey. The adulteration of milk chiefly consists in the addition of water. It may be discovered by the lowering of the specific gravity, and by the deficiency of oil-globules under the microscope.

The casein of milk may be separated by warming the liquid and adding a few drops of acetic or any other acid: in this case the casein combines with the acid (p. 637.) The action of rennet is remarkable. This substance, which consists of the inner membrane of the fourth or digesting stomach of the calf, when added to 1800 parts of milk heated to 122°, causes a perfect separation of the whole of the casein in flaky masses, a pale and yellowish watery liquid remaining, which is the whey or serum, sometimes entirely deprived of the casein. This is probably effected by the action of the organic principle, *pepsine*, (p. 655).

The watery portion, or *whey*, *i. e.* the serum of milk, is neutral, but sometimes acid. It is rendered opaline by heat, owing to the presence of albumen; also by acetic acid, if any casein remains. It has a specific gravity of 1·027, and contains 94·4 per cent. of water (*see* p. 633). It is abundantly precipitated by tannic acid and by other compounds which act on albumen. Oxalate of ammonia generally throws down a precipitate of oxalate of lime, owing to the presence of phosphate. The *butter*, or oil, which is remarkable for its fusibility at a low temperature (70°), is a compound of various fatty principles, which have been already described (p. 578). By saponification, these principles form fatty acids, including the butyric acid.

The fact that milk is the food of all young mammalia in the first stage of life, and that the growth of the body depends on the principles contained in this liquid, are sufficient proofs that casein, in the living body, can be transformed into fibrin and albumen in all their modifications; the phosphate of lime contained in milk, being appropriated for the skeleton, and the oil of milk for the production of fat.

Lactine ($C_{24}H_{24}O_{24}$, or $C_{24}H_{19}O_{19}+5HO$); *Sugar of Milk; Lactose.*—It is this substance which gives the sweet taste to fresh milk. It is procured in large crystalline masses by the evaporation of the whey of fresh milk, after the separation of the casein and oil. It is prepared in Switzerland from whey, in the manufacture of Gruyere cheese. It is white, hard, and gritty, only slightly sweet to the taste, soluble in about 6 parts of cold and 2 parts of boiling water. It does not form a syrup. It is insoluble in alcohol and ether. Its aqueous solution turns the polarized ray to the right. Dilute acids convert it into glucose. Nitric acid produces with it, oxalic, as well as mucic acid. Lactine differs from other sugars, and resembles gums, in producing the last-mentioned acid with nitric acid. It does not reduce an alkaline solution of oxide of copper, until, by the agency of an acid, it has been converted into glucose. Under these circumstances it darkens when boiled with a solution of potassa, as a result of the production of glucic acid. It readily undergoes fermentation, the casein and albumen in milk being sufficient ferments. Thus at a temperature of 104° the lactine of fresh milk is converted into alcohol and carbonic acid, by the alcoholic fermentation: if the milk has been exposed to air for some time, a change is induced in the casein, by which lactic acid is produced, as a result of the *lactic fermentation.* This is seen in the spontaneous souring of milk when long kept, the casein being separated in curds by the lactic acid, either immediately or when slightly warmed. Under other conditions milk passes through the *butyric fermentation*, and butyric acid is a product. Lactine is represented as consisting of equal equivalents of carbon, hydrogen, and oxygen; but at 248° it loses 2 atoms of water, and at 302° it loses 3 atoms of water. According to Regnault, in combining with oxide of lead, it loses 5 atoms of water: hence its formula in the anhydrous state is $C_{24}H_{19}O_{19}$. In the hydrated state it corresponds to 2 of fructose or uncrystallizable sugar, for $C_{24}H_{24}O_{24}$ are $=2(C_{12}H_{12}O_{12})$.

Lactic Acid ($C_6H_6O_6$, or $C_6H_5O_5+HO$).—This acid, which gives an acid reaction to milk, is a product of the fermentation of lactine, of beet-root juice, and other substances. It may be procured from the whey of sour milk. Sour whey is evaporated to one-sixth of its original weight and filtered: lime is added to the filtrate, to precipitate phosphoric acid, and any excess of lime is removed by oxalic acid and subsequent filtration. The liquid is concentrated, and the lactic acid may be dissolved out by alcohol, and subsequently purified. It is a colorless liquid of the consistency of syrup, miscible in all proportions with water and alcohol. It dissolves phosphate of lime, decomposes the acetates, and coagulates albumen. It produces no change in cold fresh milk, but the presence of a small trace of this acid in boiling milk, causes coagulation. It is supposed to be present in the sweat and in many of the fluids of the body. Lactic acid is simply an isomeric condition of lactine, for $4(C_6H_6O_6)=C_{24}H_{24}O_{24}$. Lactic acid contains 1 atom of water, hence its usual formula is $C_6H_5O_5,HO$.

SALIVA.—This is a transparent viscid liquid, secreted by the salivary glands. Its sp. gr. is 1·008. It is generally mixed with the mucous secretions of the mouth: these are acid, and when they predominate, give an acid reaction to the saliva, but this secretion, in a pure state, is always alkaline (ANDRAL). The alkalinity probably depends upon the presence of phosphate of soda, which with chloride of sodium and phosphate of lime, forms the bulk of the mineral matter, found in this secretion. Saliva commonly presents itself as a ropy, opaline liquid, depositing, on standing, threads or flakes of opaque mucus. Under the microscope it presents mucous globules and epithelial scales. Alcohol precipitates from the clear liquid an albuminoid principle (*ptyalin*), which forms, with the mucus, from 1 to 2 per cent. of saliva. The mucus which gives the ropiness to saliva may be separated by acetic acid. The ptyalin precipitated by alcohol is redissolved by the addition of water. The liquid is rendered more opaline on boiling, or by the action of nitric acid. Tannic acid and subacetate of lead also throw down the ptyalin. The addition of a drop of neutral persulphate of iron, imparts a deep red color to saliva, which disappears on the addition of a solution of corrosive sublimate. This indicates the presence of a trace of an alkaline sulphocyanide, which is found in all healthy saliva. The solid contents of saliva vary. We have found by experiment that the solid residue does not exceed 2 per cent. The ptyalin and mucus, according to Lehmann, are generally below 1 per cent. The saliva of tobacco-smokers, according to Gmelin, contains from 1·14 to 1·19 per cent. of solid matter, which leaves, when burned, 0·25 of ash The *tartar* which is deposited on the teeth, and *salivary calculi*, consist of the salts of the saliva, chiefly phosphate of lime cemented with animal matter.

The *ptyalin* of saliva differs from albumen in its power, at a temperature of 100°, of rapidly transforming starch and dextrine into glucose. The use of the saliva is to aid in the reduction of the food to a perfectly soft state, so that it may not only be more easily swallowed, but that when it reaches the stomach, it may be more completely penetrated by the gastric juice.

6. SERPENT-POISON; *Echidnine* (from εχὶδνοειδὴς, *viperous*).—The secretion from the poison-glands of the viper and other serpents, is a clear viscid

fluid, of a slightly yellow color, and neutral in its reaction. It contains albumen, mucus, fatty matter, a yellow coloring principle; and among its salts, phosphates and chlorides. There is associated with the albumen, a peculiar nitrogenous body resembling ptyalin and pepsine, which is called *echidnine*, and which appears to be the active poisonous principle of this fluid. Its exact constitution is unknown (BERNARD). *Echidnine* is soluble in alcohol: and may be separated from the other principles by the employment of this liquid, and subsequently evaporating the solution *in vacuo*. The fatty matter may be removed by ether. Echidnine thus obtained, is in colorless white uncrystalline scales, resembling tannic acid. It is neutral, and has neither odor nor taste. When heated with potassa, it evolves ammonia: it is soluble in water, hot and cold. The precipitate which is first produced in the aqueous solution by alcohol, is redissolved by an excess. It is not precipitated by acetate of lead. It acts upon the blood of animals like the serpent poison. De Blainville considers it to be analogous to ptyalin, and that the fluid containing it, is a peculiar kind of saliva. The poison-bag of the viper seldom contains more than one grain and a half this liquid: 1-250th of a grain is sufficient to kill a small bird. This poison produces no injurious effects when swallowed (DUMÉRIL).

7. GASTRIC JUICE.—This is a secretion from the mucous membrane of the stomach. When separated from mucus by filtration, it presents itself as a colorless limpid liquid, of an acid reaction, from the presence of lactic or hydrochloric acid, the former being probably derived from starch or sugar, taken as food. It contains from 96 to 98 per cent. of water, the residue consisting of organic matter and salts, of which chloride of sodium and alkaline sulphates are the principal. The acid mucus of the stomach is associated with a nitrogenous principle (*pepsine*), to which its solvent properties are due. It has been precipitated and extracted from the fluid portion by alcohol and acetate of lead, but probably in an altered condition. Its constituents cannot, therefore, be accurately determined. Fibrin or coagulated albumen plunged into this liquid, at the temperature of the body, swells up, and becomes gradually disintegrated and dissolved. This property of dissolving fibrin and analogous substances has been verified by experiments on animals: and in one remarkable instance in a human being, in whose stomach there was a fistulous opening. Pepsine loses this solvent property at a temperature above 120°. From the researches of Dr. Robinson on the human fœtus, it appears that no gastric juice is secreted in the stomach, until the act of respiration has been performed. He found that the contents of the stomach before birth, consisted chiefly of the liquor amnii, mixed with an albuminous matter and saliva. There is no proper digestion, and only an imperfect process of chymification.

Medicinal pepsine consists of the dried mucus scraped from the interior of the stomachs of animals (the sheep and the pig). It is sometimes incorporated with starch. The *soluble pepsine* consists of this substance dissolved in a solution of chloride of sodium. It is supposed to supply additional digestive power, to those whose stomachic secretions are deficient in pepsine.

8. PANCREATIC FLUID.—This is a colorless viscid liquid, which is secreted by the pancreas. It is always alkaline, and is rendered frothy by agitation. It yields from 8 to 9 per cent. of a solid residue, of an albuminoid nature. When heated, it sets into a solid like ovalbumen. It is also, like this principle, precipitated from its aqueous solution by alcohol; but an excess of water redissolves the precipitate, even after it has been dried. When the solid residue is incinerated, the ash yields chloride of sodium, with phosphate and carbonate of soda. The nature of the organic principle is not well

understood. It appears to resemble, in some respects, ptyalin (the albumen of saliva), but its characteristic property is to assimilate oily matters. It forms an emulsion with all oils and fats, when mixed with these substances, and the mixture is heated to about 100°,—the temperature of the body. Chemically speaking, this appears to be a process of saponification, glycerine is produced, and the fatty acids are set free.

9. MUCUS is a viscid tenacious liquid, secreted by mucous membranes in the healthy state. It is white, yellow, green, and sometimes almost black. It is thrown out from the membranes of the nose, mouth, and air-passages, as well as from the whole tract of the alimentary canal. It is sometimes opaque, at others transparent, ropy, or gelatinous, according to the part which secretes it. Mucus generally has an alkaline reaction. It is heavier than water, and insoluble, but diffusible in this liquid: it is not coagulated by heat. It is precipitated from its aqueous mixture by acetic acid and alcohol. It appears to be a modified state of albumen (*mucin*). Under the microscope, mucus presents nucleated globules and epithelial scales, which vary in shape with the situation of the membrane from which they are thrown off.

10. PUS is a morbid or diseased secretion from mucous membranes, ulcers, or abscesses. It is a creamy-looking-liquid, of a yellowish-white color. Its sp. gr. is 1·030. When in a normal state it is alkaline; and, according to Andral, it is never acid until it has been exposed to air. It contains 86·7 water, 7·4 albumen, dissolved, forming a serous liquid, and 5·9 of fatty matter, including salts. Examined microscopically, pus presents numerous white nucleated globules, mixed with oil-globules, floating in a serous liquid. When diffused in water, the serum dissolves, and the white mucous globules subside. The aqueous solution is coagulated by heat, and possesses the other properties of diluted albumen. By this character, and the presence of oil-globules, pus may be distinguished from mucus. It appears to be serum in which colorless globules of a special character are developed. If pus is mixed with a solution of potassa, it forms a jelly resembling bronchial mucus. The albuminous principle existing in pus is called *pyin*. When absorbed into the blood, pus appears to act as a powerful poison. In diseased states, of the body, it forms a vehicle for some of the most virulent animal poisons, such as that of glanders and smallpox.

11. SYNOVIA is a glairy yellowish-white fluid: it derives its name from σὺν, *cum*, and ὠὸν, *ovum*, owing to its resembling the white of an egg in its viscidity. It is secreted by the lining membranes of joints, only in sufficient quantity to keep the surfaces lubricated. It is an alkaline fluid, containing albumen and salts, which consist chiefly of the phosphates of lime and soda.

12. LIQUOR AMNII.—The organic principle in this liquid is albumen, associated with chloride of sodium and phosphate and carbonate of lime. It is remarkable that the proportion of albumen varies according to the period of gestation. At the 4th month in the human female, it amounts to 10·77 per cent.; at the 5th to 7·67; at the 6th to 6·67; and at the 9th to 0·82. In the latter stage of gestation, it contains merely traces of albumen and saline matter.

13. CUTANEOUS SECRETION. *Pulmonary exhalation.*—The sudoriparous glands of the skin, secrete a liquid which is constantly escaping in the form of vapor, and is speedily condensed on cold surfaces. Under violent exercise, or in a temperature at or above 100°, it is deposited on the skin in a liquid form: in this state it has an acid reaction. It is said to contain from 0·5

to 1·25 per cent. of a solid albuminous substance, including saline matter, principally consisting of the chlorides of sodium and ammonium, with alkaline phosphates. As it is secreted from the axillæ, it has a peculiar odor. It produces in drying a yellowish stain on linen. An aqueous solution of the dried excretion is neutral: like albumen, it is rendered opaline by boiling, and is coagulated by nitric acid. A large quantity of chloride of sodium is continually eliminated from the skin by this excretion, when the body is in a healthy state. If the hands, when perfectly clean, are dipped for a short time in distilled water, it will be found, on adding a solution of nitrate of silver to the water, that it produces a whitish precipitate, indicative of the presence of alkaline chloride derived from the skin This excretion is sometimes acid, owing to the presence of lactic and acetic acids: it easily undergoes decomposition, and sulphur compounds with ammonia and other offensive effluvia are produced. In these chemical changes of the condensed liquid, we have probably one of the sources of noxious exhalations in closely inhabited dwellings.

The *halitus*, or aqueous vapor which escapes in respiration, also contains nitrogenous animal matter, which is liable to decomposition. Ammonia is said to be thus eliminated, but we have not found this alkali present in expired air in a healthy person. When extricated from the lungs, from the blood, or from the skin, it is probably a result of the decomposition of nitrogenous matter. This exhalation generally contains noxious volatile vapors, which have been absorbed into the blood. Thus, alcohol, ether, chloroform, and prussic acid have been recognized by their odors, in the vapor expired by persons who were laboring under their effects.

Humors of the Eye.—The crystalline lens, of which the refracting index compared with that of water is 1·339 to 1·336, contains 35·9 per cent. of the albuminoid principle *globulin.* The vitreous humor consists of albumen 0·18, chloride of sodium and extractive (?) 1·43, water 98·40. The aqueous humor is water, with traces of animal matter and common salt.

Tears.—The liquid secreted by the lachrymal glands and poured from the eye under powerful emotion, is chiefly water, with a trace of albumen and chloride of sodium. The *Liquor Pericardii* and *Cerebro-spinal fluid* are also of an albuminous nature.

The two principal non-albuminous fluids produced from the blood, are the *Bile* and *Urine*—the one secreted by the venous blood of the liver, the other by the arterial blood of the kidneys.

1. Bile.—This is a ropy, viscid, and saponaceous liquid of a greenish-yellow color in man, greenish-brown in the ox, and emerald or grass-green in birds, reptiles, and fish. It has an offensive odor and a bitter taste. Its sp. gr. is 1·024. It has a slightly alkaline reaction, and it mixes in all proportions with water, giving a yellow color to this liquid, and rendering it viscid and frothy.

The bile contains no albumen: it is not coagulated by heat. Alcohol renders it turbid by precipitating the mucus. Alkalies readily mix with it; but acids, including the acetic, throw down a dense precipitate, consisting of the organic acids of the bile with mucus and coloring-matter. 100 parts of ox-bile evaporated on a water-bath left a residue of 9·2 parts solid matters, and this residue, when incinerated, yielded a strongly alkaline ash, weighing 1·2 grains. It contained a large proportion of soda.

The bile essentially consists of the salts of two peculiar organic acids, in which soda is the base, namely, the *cholate* and *choleate* of *soda*, of *cholesterine*, and fat, as well as mucus and coloring-matter. The cholic and choleic acids are of the nature of the resinous and fatty acids; hence they were formerly included under one substance, which was called biliary matter, or resin of the bile. They give, by the presence of their salts, a saponaceous character to the liquid: it is well known that ox-gall is a powerful detergent, and is much used as such, in the arts and manufactures.

By digesting the dried extract of bile in alcohol, all is dissolved excepting the mucus, the cholate and choleate of soda being soluble in this liquid. Cholic acid is a nitrogenous acid, while choleic acid not only contains nitrogen, but all the sulphur which is found in the bile. The cholic acid is in much larger proportion than the choleic.

Cholic Acid ($C_{52}H_{43}O_{12}N$) *Glycocholic, Glycocholalic Acid.*—This acid may be procured by mixing the filtered solution of bile in absolute alcohol, with three or four parts of ether. This causes a crystalline deposit of cholate of soda. By digesting this deposit in dilute sulphuric acid, crystals of cholic acid are obtained. They are very soluble in alcohol, but are not readily dissolved by water or ether. If the coloring-matter of the bile has been previously removed by animal charcoal, the crystals may be obtained quite white. Cholic acid is what has been termed a conjugated compound of a nitrogenous substance, *Glycocine* or gelatin sugar (p. 544), and a non-nitrogenous acid called the *cholalic.* When cholic acid is boiled in a solution of potassa, these compounds result, two atoms of water being required to effect the decomposition:—

$$\underbrace{C_{52}H_{43}O_{12}N}_{\text{Cholic acid.}} + \underbrace{2HO}_{\text{Water.}} = \underbrace{C_{48}H_{40}O_{10}}_{\text{Cholalic acid.}} + \underbrace{C_{4}H_{5}O_{4}N}_{\text{Glycocine.}}$$

When cholic acid is boiled with hydrochloric or other acids, glycocine is set free; but a new acid appears, namely, the *choloidic* ($C_{48}H_{39}O_{9}$). This is an isomeric compound of the anhydrous cholalic acid; in the hydrated state, the latter acid contains one equivalent of water. The choloidic acid is an uncrystalline resinous-looking substance, insoluble in water and soluble in alcohol, like a resin. This was no doubt the resin of the bile as described by former writers. Cholalic acid, when long boiled with hydrochloric acid, is itself decomposed: it loses three equivalents of water, becoming *Dyslysine* ($C_{48}H_{36}O_{6}$).

Choleic Acid ($C_{52}H_{45}O_{14}S_{2}N$). *Tauro-cholic. Tauro-cholalic Acid.*—This acid is procured from the choleate of soda, by adding acetate of lead to a solution of bile in 10 or 15 parts of water, and afterwards a little ammonia. The resulting precipitate is gently heated; the liquid is then poured from it, and it is triturated and washed with a little water, and afterwards treated with boiling alcohol, which dissolves an acid salt, leaving a basic salt, and a compound of coloring-matter and oxide of lead. The alcoholic solution, decomposed by sulphuretted hydrogen, filtered, and evaporated to dryness, leaves a brown resinous magma, from which fatty matters (margaric acid and cholesterine) must be separated by ether: it is then redissolved in cold weak alcohol, filtered and evaporated to dryness: the remaining choleic acid is slightly contaminated by soda, sulphur, and margaric acid. (DEMARÇAY.) It has not yet been obtained in a pure state; but its constitution may be inferred from the compounds into which it is resolved, when boiled with alkalies, namely, *taurine* and *cholalic acid.* Two equivalents of water are required to bring about this change, when choleic acid is boiled in a solution of potassa:—

$$\underbrace{C_{52}H_{45}O_{14}S_{2}N}_{\text{Choleic acid.}} + \underbrace{2HO}_{\text{Water.}} = \underbrace{C_{48}H_{40}O_{10}}_{\text{Cholalic acid.}} + \underbrace{C_{4}H_{7}O_{6}S_{2}N}_{\text{Taurine.}}$$

It is remarkable that in this breaking-up of choleic acid, all the sulphur and nitrogen should go into the taurine. Acids produce a similar change, but they convert the cholalic into *choloidic acid;* and this, by further boiling, into dyslysine. It appears that when the bile is spontaneously changed by putrefaction, taurine and cholalic acids, are products of the decomposition of the cholic and choleic acids.

The impure cholic and choleic acids, as they are obtained in combination with soda, by the evaporation of bile, form a greenish-brown resinous-looking substance, which melts like a resin, burns with a smoky flame, and leaves a carbonaceous ash, in which soda may be abundantly detected. It was formerly called *Bilin.*

Taurine ($C_4H_7O_6S_2N$).—This principle is obtained directly from bile, by boiling it with hydrochloric acid until the liquor, at first turbid, becomes clear: the choloidic acid is separated by decantation, and the liquid is evaporated until the greater part of the chloride of sodium has been deposited. Five or six parts of alcohol are then added to the mother-liquor, when the taurine gradually falls in acicular crystals, which may be purified by washing them with alcohol, solution in boiling water, and recrystallization. Pure taurine forms colorless four-sided prisms, which are inodorous and nearly tasteless, neutral, permanent in the air, soluble in water, but insoluble in absolute alcohol. The presence of a large amount of sulphur in taurine (and in bile) is important in reference to chemical physiology, and the functions of the liver. A variety of other products have been described as derivatives from bile, but they have not been adequately defined or examined. Some of them appear to be the preceding substances in an impure state, or mixtures of them.

Cholesterine ($C_{52}H_{44}O_2+2HO$).—This is a solid fatty principle, found in traces only in the bile: according to Berzelius, it does not form more than one-10,000th part of this liquid. It cannot be readily extracted from bile, but it may be procured from *gall-stones.* These consist of cholesterine (*χολή, bile,* and *στέαρ, fat*), or inspissated bile, with mucus and more or less coloring matter. These stones are lighter than water, of various colors, generally brittle, friable, with flat surfaces and angles. When heated, they melt and burn. To obtain cholesterine, the gall-stone is finely powdered, and the powder boiled in alcohol. The liquid is filtered while hot, and on cooling, the cholesterine is deposited in pearly scales. Cholesterine has been found in the brain, in yelk of egg, and in some morbid secretions.

Pure cholesterine is seen in colorless scales, which are lighter than water, and fusible at 293° into a colorless liquid, which does not concrete until cooled to 240°. It is insoluble in water, and scarcely soluble in cold alcohol; it dissolves in boiling alcohol, ether, wood-spirit, and in oils. In close vessels, it may be sublimed unchanged. It is not acted upon by the alkalies even when long boiled in their solutions.

In addition to cholesterine, there is a peculiar fatty matter in bile in combination with soda. It exists as margarate and oleate of soda.

Lithofellic Acid ($C_{40}H_{35}O_7,HO$).—This compound resembles cholesterine in its properties. It is found in the form of brown concretions in the intestines of certain animals in eastern countries. The concretions are known under the name of *bezoars.*

Ambreine ($C_{36}H_{32}O$).—This is obtained from ambergris, which is a diseased concretion from the intestines of the spermaceti whale. It is a fat-like matter, amounting, in some specimens, to 60 per cent., and, according to Chevreul, it resembles cholesterine. Benzoic acid has been found in some specimens of ambergris; in others, equally genuine, there are no traces of it. *Musk, castor,* and *civet,* exclusive of their peculiar and odorous principles, contain distinct species of fat.

Tests for Bile.—1. The cholates and choleates may be distinguished by the peculiar action of sulphuric acid and grape-sugar upon their solutions, moderately heated. (PETTENKOFER.) If to half an ounce of diluted bile, one drop of a solution of sugar is added, and sulphuric acid is gradually dropped into the mixture, a brownish precipitate is at first formed; but this is dissolved on the addition of more acid, and the liquid acquires a rich red, gradually passing into a purple color. It is brought out by warming and agitating the mixture, taking care that the temperature does not exceed 120°. The color is strikingly shown by heating the mixture in a white plate.

2. The coloring-matter of bile, when diluted with water, appears yellow: it imparts a yellow stain to organic substances. Strong nitric acid produces with it a green color, passing through shades of blue, violet, and red, under exposure to air, the intensity of the colors depending on the quantity present. Nitric acid dropped on bile, rendered a little alkaline, produces a red and bluish, followed by a green color. One mode of testing for diluted bile in liquids is dependent on this reaction. Add a small quantity of nitric acid to the liquid and allow it to stand. The liquid slowly acquires a greenish color if the coloring-matter of bile is present. The green color is strikingly brought out by adding strong hydrochloric acid to the colored liquid, and boiling the mixture for a short time. The production of a green color by acids, merely indicates the presence of the coloring-matter—not of the bile itself. The only true test for bile, is that of Pettenkofer: the production of a red color by the action of sulphuric acid and sugar, indicates the presence of cholic and choleic acids. It has been noticed in certain cases, that the urine contained the coloring-matter only: it was turned green by nitric acid, but as it gave no results with the sulphuric acid and sugar-tests, the main constituents of the bile were absent.

We subjoin, in a concise form, an analysis of 100 parts of the bile of the ox, sp. gr. 1·024:—

Cholic and choleic acids, with mucus and fat	8·0
Mineral matter containing much soda	1·2
Water	90·8
	100·0

The action of the bile in chymification in the living body, does not admit of any satisfactory chemical explanation. It assists in some manner to convert the chyme (digested food) into chylous matter, rendering it proper for absorption and for being carried into the blood.

The *meconium* which collects in the intestines during fœtal life has been found to consist chiefly of excreted bile with intestinal mucus.

Excrementitious matter.—This has been supposed to consist, in great part, of biliary matter; but from analyses which have been made, it appears that, except under the violent action of purgative medicines or in disease, the amount of bile actually discharged, is very small. The portion which is excreted, consists chiefly of the coloring and fatty matters, and does not amount to more than one-sixteenth part of the weight of the secretion. Hence the organic acids of the bile, are probably reabsorbed into the system in an altered condition. The proportion of water in feculent matter is about 70 to 75 per cent., and the residue is made up of unassimilated food, woody fibre, and nitrogenous matters. Dr. Marcet has extracted from feces a crystalline principle which he calls *Excretine.*

An analysis made by Berzelius gives the following results: Water 73·3; soluble organic matters, including bile, albumen, and salts, 5·7; insoluble residue of food, 7·0; insoluble matters from the intestines, with mucus, 14. The salts are chiefly phosphates and chlorides.

2. The URINE.—This liquid, which is secreted by the kidneys, carries off several substances from the blood, which may be termed excrementitious, and which would be injurious if retained: these substances, for the most part, abound in nitrogen. Its sp. gr. ranges from 1·015 to 1·030. It is usually about 1·020; but in some forms of disease it is found to be much higher, and in others, much lower.

The urine when first voided is limpid, and of various tints of yellow, inclining in health to a pale straw-color. Its taste is saline and bitterish. Its odor is peculiar, urinous. Its solid contents may in general be estimated at between 5 and 8 per cent.

Recent healthy urine almost always has more or less of an acid reaction. According to Andral, the urine is acid in health and disease; and is only alkaline, when the mucous membrane secretes pus. After it has stood in an open vessel for a few hours, the acidity gradually becomes less apparent, and it generally deposits a little mucus, containing traces of acid urate of ammonia. It is extremely prone to complicated changes; and in warm weather it begins in the course of a few hours to putrefy and to acquire new properties. It becomes alkaline, acquires a disagreeable odor, and lets fall a whitish, sediment, consisting chiefly of ammonio-magnesian phosphate, and phosphate of lime; it becomes afterwards ammoniacal, and is found to hold carbonate of ammonia in solution. Similar changes may be effected by continued boiling; they are chiefly referable to the decomposition of the characteristic ingredient of the urine, namely *urea*, a substance which is easily resolved during putrefaction into carbonate of ammonia.

The principal constituents of healthy urine are *urea*, *uric acid*, *fixed salts*, *coloring-matter*, organic matters, and *mucus*. As the urine varies in sp. gr., so do these substances vary in quantity; and in the same individual, at different hours of the day, the urine presents very different proportions of solid contents. The late Dr. Golding Bird obtained the following results, in examining 1000 parts of the urine of a healthy person after ten hour's fasting, (*urina sanguinis*), and the urine after dinner in the evening (*urina cibi*):—

Analysis of urine.	After fasting.	After eating.
Specific gravity	1·016	1·030
Water	962·72	930·10
Solids	37·28	69·90
Urea	14·30	24·40
Uric acid	0·23	1·33
Fixed salts, chiefly chlorides, sulphates, and phosphates	5·10	9·90
Organic matter, kreatine, kreatinine, coloring matter, and volatile salts	17·80	34·27

The acidity of fresh urine has been variously ascribed to the presence of uric acid, of hippuric acid, of lactic acid, and superphosphates. It is probable that it depends on the presence of the latter.

The properties and composition of the salts found in the urine, have already been described in other parts of the work. The chemical properties of *urea*, and of *uric acid*, bodies which peculiarly characterize urine, remain to be noticed.

UREA ($C_2H_4O_2N_2$).—This is the principle which confers upon the urine its chief peculiarities. It may be procured by the following processes:—(1.)Evaporate urine by a gentle heat (never exceeding 200°), to the consistence of a thin syrup, filter, and add to the filtrate, an equal volume of colorless nitric acid, (sp. gr. 1·35), which should be perfectly free from nitrous acid. A brisk effervescence ensues, and there is at the same time a copious deposition of crystallized and nearly pure nitrate of urea, this compound not being dissolved by an excess of strong nitric acid. If the evaporated urine is allowed to cool before the acid is added, the crystals are very brown. The nitrate of urea is dissolved in a small quantity of water, and treated with carbonate of baryta or of potassa, until rendered neutral: on evaporating the clear solution, crystals of nitrate of baryta (or nitrate of potassa), are first obtained, and then those of urea. The latter are purified by redissolving them in alcohol, which takes up the urea, and yields it in crystals, when evaporated. If the urea is colored, a little permanganate of potassa may be added to its aqueous solution, which has no action on urea, but destroys the coloring-matter. Any color communicated by an excess of permanganate, is instantly destroyed by a few drops of alcohol, and the filtrate then yields colorless crystals of urea. (2.) The concentrated urine may be saturated by oxalic acid, which yields crystals of oxalate of urea; these, dissolved in water, decolored by animal charcoal, and decomposed by digestion with carbonate of lime, yield a solution from which colorless crystals of urea may be obtained. (3.) From *cyanate of ammonia.* 28 parts of dried ferrocyanide of potassium, and 14 parts of binoxide of manganese, are mixed in powder, and calcined upon an iron plate, heated to dull redness; the mixture takes fire, but is gradually extinguished, and must be stirred, while cooling, to prevent agglutination. The cold mass is then powdered and digested in cold water, which takes up the cyanate of potassa; this solution is filtered off and set aside; the remaining powder is then washed with a second portion of cold water and again filtered, and in this filtrate, 20·5 parts of sulphate of ammonia are dissolved, and the solution added to the first filtered solution of the cyanate. A large quantity of sulphate of potassa is deposited, which is strained off, and the filtered liquor, now containing, with some sulphate of potassa, all the cyanate of ammonia, is evaporated to dryness, during which process the cyanate of ammonia is transformed into urea (p. 18). The dry mass is digested in alcohol, which dissolves only the urea, and yields it pure, on evaporation. (LIEBIG, *Annalen der Pharm.*, xxxiii. 108.)

Urea crystallizes in flattened four-sided prisms; they generally resemble nitre in appearance, and have a similar cooling saline taste: they are inodorous. They are soluble in their own weight of cold water, and in every proportion in hot water; they dissolve in 4·5 of cold, and in 2 parts of boiling alcohol; but they are insoluble in ether, and in an excess of strong nitric acid. Their solution is neither acid nor alkaline; but urea belongs to the class of neutral organic bases, and forms crystallizable compounds with several of the acids. Pure urea is permanent in the air; at 250° it fuses into a colorless liquid; at a higher temperature it yields ammonia, cyanate of ammonia, and dry solid cyanuric acid. When heated in hermetically sealed vessels to between 428° and 464°, it is entirely converted into carbonate of ammonia. Alkalies do not evolve ammonia by their action upon urea, unless aided by heat; but when fused with them it is resolved into carbonic acid and ammonia. An aqueous solution of urea remains long without change; but the addition of proteiniferous substances resolves it more rapidly into carbonate of ammonia. In this case 1 atom of urea, and 2 atoms of water, yield 2 atoms of carbonate of ammonia: $C_2H_4O_2N_2, + 2HO, = 2(NH_3, CO_2)$. Urea produces no precipitate in a solution of nitrate of silver; but when nitrate of silver and a little potassa are added to a cold solution of urea, a compound of oxide of silver with urea, is thrown down. If the mixed solution of urea and silver is evaporated at about 120°, nitrate of ammonia and cyanate of silver are the results; an atom of urea containing the elements of an atom of cyanic acid, an atom of ammonia, and an atom of water: $C_2H_4O_2N_2=NC_2O,+NH_3,+HO$.

Nitrate of Urea ($C_2H_4O_2N_2,NO_5HO$).—This is prepared by the process above described. It crystallizes in rhombic plates. The crystals are soluble in 8 parts of cold water. Heated above 212°, nitrate of urea is decomposed, evolving carbonic acid and nitrogen. At 284° it is resolved, according to Pelouze, into carbonic acid and nitrous oxide, in the proportion of 2 volumes to 1, and the residue is nitrate of ammonia; at a higher temperature, water, nitrous oxide, carbonic acid, and ammonia, are the products.

Nitrous acid immediately decomposes urea; equal volumes of carbonic acid and nitrogen are evolved, and nitrate of ammonia is formed: ($C_2H_4O_2N_2+2NO_4=2CO_2+2N+NH_4O,NO_5$). (MILLON, *Ann. Ch. et Ph.*, 3ème Sér. viii. 233.)

Oxalate of Urea ($C_2H_4O_2N_2+C_2O_3+HO$).—This salt is thrown down in short flattened prismatic crystals, on mixing strong aqueous solutions of oxalic acid and urea: it is less soluble than the nitrate. The production of the nitrate and oxalate can be well observed under the microscope with an inch power, on adding the respective acids to concentrated urine.

Sal-ammoniac crystallizes from an aqueous solution containing a little urea, in cubes instead of octahedra; while common salt, under the same circumstances, crystallizes in octahedra instead of cubes: these crystals only contain a trace of urea.

The proportion of urea contained in urine, is subject to great variation. Sometimes it can scarcely be detected, owing to the large amount of other organic matters which are present (diabetes). It is deficient in hysteria. It is generally in larger quantity in the urine of males, than in that of females, and is more abundant in youth than in old age. It is the great medium for the elimination of nitrogen, of which it contains 28 per cent. It is found in the healthy blood in small quantity, so that it appears to be simply eliminated, and not secreted by the kidneys. When these organs are extensively diseased, the urea accumulates in the blood, and is found in large quantity in this and other fluids of the body. It then produces a form of narcotic poisoning, known under the name of *uræmia.*

In a state of health, human urine does not contain sufficient urea to be indicated by a deposit of crystals, on the addition of nitric acid; but if fresh urine is gently evaporated in a watch-glass to about one-third of its bulk, and an equal volume of strong colorless nitric acid is then added, there should be, after a time, a deposit of crystallized nitrate of urea in rhombic plates.

URIC ACID ($C_{10}H_4O_6N_4=C_{10}H_2O_4N_4+2HO$). *Lithic Acid. Urylic Acid.*—This acid forms but a small proportion of the solid contents of urine. It is found abundantly in some kinds of urinary calculi (hence called *lithic acid*), in the urine of birds of prey, and those which feed on fish and animal matter. The substance called *Guano*, which is used as a *manure*, is the decomposed excrement of aquatic birds; it contains a large proportion of uric acid. The excrement of birds, generally consists of a white chalky mass which is a compound of uric acid and lime. The excrement of the boa-constrictor and other large snakes is chiefly composed of urate of ammonia; it is voided in the form of a gray semi-fluid mass, which, on drying, forms a whitish, friable, chalky-looking substance. In order to procure pure uric acid, this substance should be reduced to powder and boiled, first in alcohol, and then in water, to remove all matters soluble in these liquids; it may then be treated with dilute hydrochloric acid to remove phosphate of lime, washed, and digested in a hot solution of caustic potassa. The liquid is then poured off or filtered, more of the solution of potassa is added to it, and it is concentrated by evaporation, when the urate of potassa, which is not soluble in the strong alkaline liquid, separates, while the coloring matters are retained. On cooling, the whole concretes into a pasty mass, which must be pressed out and washed with cold water. The urate of potassa which remains, is then dissolved in boiling water, and the hot solution poured into hydrochloric acid, when a white gelatinous precipitate falls, which soon assumes a crystalline aspect, and when washed and dried, is pure uric acid.

Uric acid may be also obtained by boiling the excrement of the snake in 30 or 40 parts of a weak solution of caustic potassa until the odor of ammonia is no longer perceived; the solution is then filtered, and hydrochloric acid is added.

Uric acid is a soft white crystalline powder; it is insipid and inodorous; it slightly reddens moistened litmus-paper. It is almost insoluble in cold water, requiring 10,000 parts to dissolve it, but soluble in between 1800 to 1900 parts of boiling water; it is insoluble in alcohol and in ether. Sulphuric acid dissolves it, but it is again precipitated as a hydrate on adding water. It is dissolved by potassa and soda, but not by their carbonates. When dried at 212°, this acid retains two atoms of water, being bibasic; $C_{10}H_2O_4N_4+2HO$. When heated on platinum foil, the acid is decomposed, leaving only a slight residue of carbon. If heated in a close tube, it evolves, among other products, ammonia.

Owing to the small quantity present in urine, it is not easily detected in this liquid. It may, however, be discovered by the use of the microscope. As it exists in the urine in a combined state, an acid must be employed for its separation. Two or three ounces of urine should be warmed and poured into a conical test-glass; a few drops of hydrochloric acid are added, and the liquid stirred. After some hours, either a dark-colored pellicle forms on the surface, or small reddish-brown crystals are deposited. These, when examined microscopically, have a rhombic or fascicular form. They are combined with much coloring matter. Uric acid has been found as urate of soda, in the blood of gouty persons. It is observed that the proportion of uric acid is diminished in the urine, immediately before a paroxysm of gout.

Tests for the Acid.—In addition to the chemical characters above mentioned, uric acid may be identified by the peculiar action of nitric acid. The powdered acid dissolves with effervescence in nitric acid. The solution is gently evaporated at a low temperature, and when the excess of nitric acid has been expelled, and the yellowish-colored residue has been exposed to the vapor of ammonia, the rich purple color of purpurate of ammonia, or murexide, appears. (*See* p. 624).

Urates.—All the *urates* are sparingly soluble in cold water, and they are mostly, white insipid powders. By dry distillation they yield carbonate and hydrocyanate of ammonia, cyanic acid, and an empyreumatic oil; and those with alkaline bases leave cyanides. They are more soluble in boiling water.

Acid Urate of Ammonia ($NH_4O,HO,C_{10}H_2O_4N_4$).—When uric acid is digested in a solution of caustic ammonia, it becomes warm, and increases in bulk, forming, when dried, a white, amorphous salt, scarcely soluble in cold water. It may be obtained in minute acicular crystals, by adding excess of ammonia to a boiling mixture of uric acid and water, and when dried at 100°, has the above composition. It requires 1608 parts of water at 60° for its solution. When long boiled in water, it is decomposed, ammonia is evolved, and the pure acid remains. This compound forms one variety of urinary calculus (stone), and is frequently deposited from urine as a reddish-brown sediment, soluble in the hot liquid, but precipitated on cooling.

Urate of soda constitutes what are termed chalk-stones, which are deposited in the joints of the fingers in gout.

The action of *nitric acid* upon *uric acid* is attended with the production of some remarkable compounds. When 1 part of uric acid is added by small portions at a time to 2 parts of nitric acid (sp. gr. 1·41 to 1·45), care being taken to prevent the heating of the mixture, nitrogen and carbonic acid (in equal volumes) are evolved, and the mixture becomes a crystalline magma, from the formation of *alloxan* ($C_8H_4O_{10}N_2$). Nitrate of urea is probably first formed, which is decomposed by the evolved hyponitrous acid, and nitrate of ammonia, carbonic acid, and nitrogen are produced. If the nitric acid, instead of being concentrated, is very dilute, the uric acid dissolves with effervescence, and *alloxantine* ($C_8H_5O_{10}N_2$), nitrate of ammonia, and nitrate of urea, are found in solution. If uric acid is dissolved in moderately strong nitric acid, and the liquid is evaporated until gas is no longer evolved, the alloxan originally produced, is decomposed; and crystals of *parabanic acid* ($C_6H_2O_6N_2$) are formed. When the solution of parabanic acid is supersaturated with ammonia and evaporated, it combines with the elements of water to form *oxaluric acid*, $=C_6H_4O_8N_2$. If the nitric solution of parabanic acid, instead of being saturated with ammonia, is further evaporated, it continues to evolve carbonic acid, and ultimately yields crystals of *nitrate of urea.* When a solution of uric acid in very dilute nitric acid, is evaporated until the alloxantine which it contains, crystallizes, and the residue is saturated with ammonia, the liquid acquires a purple color, and deposits *murexide*, together with a red powder, which is *uramile* ($C_8H_5O_6N_3$). (p. 624.)

HIPPURIC ACID. *Uro-benzoic Acid* ($C_{18}H_9O_6N$).—The properties of this acid and the method of procuring it have been elsewhere described (p. 602). It appears to have been for a long time mistaken for benzoic acid in the urine of the cow, horse, and other herbivora. It will be only necessary here to describe the method of detecting the acid in urine. A few ounces should be evaporated to a small bulk and an equal bulk of hydrochloric acid then added. A mixture of hippuric and uric acids slowly falls mixed with coloring-matter. The supernatant liquid being decanted, the deposit should be boiled in alcohol, in which hippuric acid alone is soluble. As it is obtained from the alcoholic solution, it presents itself in four-sided prisms with pointed terminations.

The *Coloring-matter* of the urine has not been separated in a distinct form. Heller has called it *Uroxanthin.* The late Dr. Bird suggested a test for this principle. A small quantity of urine is heated in a tube to the boiling-point, and a few drops of hydrochloric acid are added. The color produced varies from a pale lilac to a deep crimson, according to the amount of coloring-matter present. A substance analogous to indigo has been occasionally found in this liquid: we have in one instance seen the urine of a deep purple-black color. In hysteria the coloring-matter is frequently in very small proportion.

Mucus.—This presents itself in healthy urine as a faint cloud subsiding after some hours to the bottom of the vessel. It may be separated by filtration.

Kreatine and *Kreatinine* may be detected by the process recommended by Dr. Bird. Evaporate an ounce of urine and allow it to cool. Decant the fluid extract from the deposited salts. Dissolve in the extract, a piece of chloride of zinc about the size of a pea, and set the whole aside for twenty-four hours. When the residue is examined by the microscope, radiating crystals like minute zeolites, will be observed, consisting of a triple compound of zinc and chlorine with kreatine and kreatinine. Their crystalline form is more distinctly seen, by dissolving them in a drop of water on a glass slide over a spirit-lamp, and allowing the solution to evaporate spontaneously.

In reference to the *fixed salts*, it may be observed that ammonia or lime-water added to urine, produces a white precipitate, by neutralizing the excess of acid and throwing down the earthy phosphates. A salt of baryta (with nitric acid) gives a dense precipitate indicative of the presence of much *sulphuric acid:* nitrate of silver (with nitric acid) throws down an abundance of chloride (*chlorine*), and oxalate of ammonia precipitates *lime* from the lime-salts dissolved in the liquid. Under the microscope, this deposit, if slowly formed, appears in the shape of octahedral crystals with a square base (*oxalate of lime*).

The ash of urine indicates by the usual tests, the presence not only of lime, but of *soda*, which exists chiefly as chloride of sodium. The presence of *magnesia* in urine is indicated by the stellated crystals of *phosphate of ammonia and magnesia*, which are seen under the microscope, on adding ammonia to a few drops of urine on a microscopic slide. By evaporating the urine (after fasting) *chloride of sodium* may be seen in the form of crosses and daggers mixed with plumose crystals of phosphate of soda.

The *abnormal* ingredients in the urine, are very numerous. *Albumen* may be detected by the turbidness or coagulum produced on heating the liquid, as well as by the action of nitric acid. Albuminous urine is frothy and of low specific gravity. *Pus* may be detected in the sediment, by the presence of oil-globules, also of albumen in the urine, and by the production of a jelly-like mass, on adding to the sediment an equal volume of solution of potassa. *Blood* may be distinguished by a smoky color, if in small quantity, or by a reddish color, if in large proportion. The urine also contains the albumen of serum. *Sugar* may be detected by evaporating the urine to a syrup, digesting the residue in boiling alcohol, and testing the alcoholic extract by the copper test. (*See* p. 528.)

URINARY CALCULI.—These usually include—1. Uric acid; 2. Urate of ammonia; 3. Oxalate of lime; 4. Phosphate of lime, and 5. Phosphate of ammonia and magnesia. The first two may be distinguished by the action of nitric acid. (*See* p. 664.) For the method of detecting insoluble phosphates, see p. 227: and for the analysis of oxalate of lime, p. 593.

APPENDIX.

WEIGHTS AND MEASURES.

THE subject of weights may be regarded as being at present in a transition state. The Medical Council, in bringing out the new British Pharmacopœia for the three kingdoms, have proposed to substitute the Avoirdupois for the Troy pound but to retain the Avoirdupois ounce, and to divide it into 480 parts or grains, so that there may be *nominally* the same number of grains to drachms and scruples. The Avoirdupois ounce, however, represents only 437·5 grains in Troy or Apothecaries' weight, hence this further subdivision, would reduce the value of the *grain* now used in medicine and chemistry by 1-11th part and a fraction. Drachms and scruples would be reduced in similar proportion. The Royal College of Physicians have resisted this innovation as inexpedient, and liable to lead to great confusion in the compounding of medicines.

On the other hand, a select Parliamentary Committee has recently advised in a Report, that the ordinary English weights should be abolished, and the metrical system of the French, adopted in place of them. "The only weights and measures in use, should be the metric and Imperial, until the metric has been generally adopted." (*Report*, Sept. 1862.)

In the meantime, we subjoin tables of English weights and measures as they are now used in science and commerce. In these, the reader will find the subdivisions of the two English pounds, with their equivalents in French grammes, on the metrical system.

The two systems of weights called *Troy* and *Avoirdupois* have no common integer except the *grain.* Although the names, pound, ounce, and drachm are common to both systems, they denote different quantities in each. The English *Troy* pound is subdivided into twelve ounces, and each ounce is equal to 480 grains. The subdivisions of the Troy ounce, called *Apothecaries' weight,* are into 8 drachms, each drachm into 3 scruples, and each scruple into 20 grains. The Troy ounce is also divided into 20 pennyweights, of 24 grains each. These are the weights generally employed; but for philosophical purposes, ambiguity is most easily avoided by employing the *grain* as integer: and the Laboratory should be provided with good sets of weights, from 1000 grains downwards; the grain should be decimally subdivided into tenths, hundredths, and thousandths.

APOTHECARIES' WEIGHT.

Pound.		Ounces.		Drachms.		Scruples.		Grains.		French grammes.
1	=	12	=	96	=	288	=	5760	=	372·96
		1	=	8	=	24	=	480	=	31·08
				1	=	3	=	60	=	3·885
						1	=	20	=	1·295
								1	=	0·0647

AVOIRDUPOIS WEIGHT.

Pound.		Ounces.		Drachms.		Grains.		French grammes.
1	=	16	=	256	=	7000	=	453·25
		1	=	16	=	437·5	=	28·328
				1	=	27·343	=	1·77

Measures of Volume.—Weights are connected with measures by the subdivisions of the Imperial gallon. The weight of an Imperial gallon of absolutely pure water, at 30 inches pressure, and 62°, is *ten Avoirdupois pounds*, or 70,000 grains. It is equal to 277·274 cubic inches. It is one-fifth more than the old Wine gallon, *i. e.* 30 Imperial are=36 Wine gallons.

IMPERIAL MEASURE.

Gallon.		Pints.		Fluidounces.		Fluidrachms.		Minims.
1	=	8	=	160	=	1280	=	76800
		1	=	20	=	160	=	9600
				1	=	8	=	480
						1	=	60

WEIGHT OF WATER AT 62°.

Measure.		Cubic inches.		Grains.
1 Gallon	=	277·274	=	70,000
1 Quart	=	69·318	=	17,500
1 Pint	=	34·659	=	8,750
16 Fluidounces	=	27·727	=	7,000
1 Fluidounce	=	1·732	=	437·5
1 Fluidrachm	=	0·216	=	54·7
1 Minim	=	0·0336	=	0·91

The weight of *one cubic inch* of distilled water at 62° is 252·458 grains. The Troy ounce of distilled water, which contains 480 grains, is equal to 1·8047 cubic inches. The wine-pint corresponds to 28·875, and the Imperial pint to 34·65 cubic inches at 60°.

THE METRICAL SYSTEM.—The French metre is equal to 39·370788 English inches. The *metre* is in France the integer of the measure of *length*, and from it all measures of surface, capacity, and weight, are derived. The integer of the measure of capacity, is the *litre*, which is the cubed decimetre, and is equal to 35·275 fluidounces, or 1·763 Imperial pints. The integer of the measure of weight, is the *gramme*,=15·434 English grains. It is exactly equal to the weight of a *cubic centimetre* of water weighed *in vacuo*, at its maximum density (39°·38). The cubic centimetre is employed by French chemists in all measurements of gases in place of our cubic inch. It is equal to 0·061 of a cubic inch. The weight of the cubic centimetre of water, is to the cubic inch of water, as 15·434 to 252·458 : hence there are 16·34 cubic centimetres to an English cubic inch.

This rule is sufficiently correct for practical purposes. It is to be observed, however, that the French take the weight of the cubic centimetre of water at 39·38 *in vacuo :* the English take the weight of the cubic inch (252·458 grains) at 62° in air. Assuming the sp. gr. of water at 32°, to be 1·000000, the sp. gr. at 36°·38 is to the sp. gr. at 62°, as 1·000099 to 0·999000.

The French measures increase and decrease in decimal proportions. For the *increase*, a prefix is used, derived from the Greek *deca*, *hecto*, *kilo*, and *myria ;* the integer, whether metre, litre, or gramme, being multiplied by 10, 100, 1000 and 10,000 respectively. To indicate the *decrease*, the prefixes *deci*, *centi*, and *milli*, derived from the Latin, are employed. In this case the integer is supposed to be divided by 10, 100, or 1000.

Various plans have been devised for converting the French weights and measures into their English equivalents. The following Tables will be found useful for this purpose :—

MEASURES OF LENGTH.

		English inches.
Millimètre	=	·03937
Centimètre	=	·39371
Decimètre	=	3·93708
Mètre	=	39·37079
Decamètre	=	393·70788
Hectomètre	=	3937·0788
Kilomètre	=	39370·788
Myriamètre	=	393707·88

MEASURES OF VOLUME.

		Cubic inches.
Millilitre	=	·06103
Centilitre	=	·61028
Decilitre	=	6·1028
Litre	=	61·028
Decalitre	=	610·28
Hectolitre	=	6102·8
Kilolitre	=	61028·
Myrialitre	=	610280·

MEASURES OF WEIGHT.

		English grains.
Milligramme	=	·0154
Centigramme	=	·1543
Decigramme	=	1·5434
Gramme	=	15·434
Decagramme	=	154·34
Hectogramme	=	1543·4
Kilogramme	=	15434·
Myriagramme	=	154340·

A kilogramme is equal to 2·2046 pounds Avoirdupois, and 1000 kilogrammes are equal to an English ton. The quintal, or 50 kilogrammes, is equal to the English cwt. With respect to the equivalents of French and English weights and measures, some slight differences will be found among English writers. These arise from the calculations being based on the employment of a larger or smaller number of decimal figures.

Surfaces and Capacities.—*Surface of a Sphere:* diameter squared × 3·141593. *Capacity of a Sphere:* diameter cubed × 0·5236. *Area of a Circle:* diameter squared × 0·785938. *Area of Rectangle, Square, Rhombus, and Rhomboid:* base × by the height. *Capacity of the Prism or Cylinder.* (Rule for calculating the capacities of cylindrical vessels used for Gases :) area of the base × by height.

Barometric Scale in Millimetres and Inches.

In foreign scientific works, the barometrical pressure, whether for meteorological or other scientific purposes, is represented in millimetres. The subjoined Table gives the corresponding equivalents in English inches : the pressure to which gases are submitted, may be thus easily ascertained without resorting to calculation : 762 mm = 30 inches mean pressure.

Mm.		In.	Mm.		In.	Mm.		In.
700	=	27·560	730	=	28·741	760	=	29·922
701	=	27·590	731	=	28·780	761	=	29·961
702	=	27·638	732	=	28·819	*762	=	*30·000
703	=	27·678	733	=	28·859	763	=	30·040
704	=	27·717	734	=	28·898	764	=	30·079
705	=	27·756	735	=	28·938	765	=	30·119
706	=	27·795	736	=	28·977	766	=	30·158
707	=	27·835	737	=	29·016	767	=	30·197
708	=	27·876	738	=	29·056	768	=	30·237
709	=	27·914	739	=	29·095	769	=	30·276
710	=	27·953	740	=	29·134	770	=	30·315
711	=	27·992	741	=	29·174	771	=	30·355
712	=	28·032	742	=	29·213	772	=	30·384
713	=	28·071	743	=	29·252	773	=	30·434
714	=	28·111	744	=	29·292	774	=	30·473
715	=	28·150	745	=	29·331	775	=	30·512
716	=	28·189	746	=	29·371	776	=	30·552
717	=	28·229	747	=	29·410	777	=	30·591
718	=	28·268	748	=	29·449	778	=	30·631
719	=	28·308	749	=	29·489	779	=	30·670
720	=	28·347	750	=	29·528	780	=	30·709
721	=	28·386	751	=	29·567	781	=	30·749
722	=	28·426	752	=	29·607	782	=	30·788
723	=	28·465	753	=	29·646	783	=	30·827
724	=	28·504	754	=	29·685	784	=	30·867
725	=	28·543	755	=	29·725	785	=	30·906
726	=	28·583	756	=	29·764	786	=	30·945
727	=	28·622	757	=	29·804	787	=	30·985
728	=	28·661	758	=	29·843	788	=	31·024
729	=	28·701	759	=	29·882	789	=	31·063

THERMOMETRICAL EQUIVALENTS.

Rules for converting Degrees of Fahrenheit's, Centigrade, and Reaumur's Thermometers into each other.

The space between the two fixed points of temperature—namely, the freezing and boiling of water, is divided by Fahrenheit into 180°, by Centigrade into 100°, and by Reaumur into 80° :—

$\frac{180}{20} = 9.\ \frac{100}{20} = 5.\ \frac{80}{20} = 4$: therefore 9 F. represents 5 C. and 4 R.

$$\left.\begin{array}{l}5 \times 1{\cdot}8 = 9\\ 9 \div 1{\cdot}8 = 5\end{array}\right\}\text{ therefore }\begin{array}{l}\text{C.} \times 1{\cdot}8 = \text{F.}\\ \text{F.} \div 1{\cdot}8 = \text{C.}\end{array}$$

The zero of C. and of R. is at the freezing of water : the zero of F. is 32° F. below the zero of C. and of R.

Therefore—1. For temperatures *above* the zero of C. (32° F.)

Rule.	*Examples.*
F. — 32 ÷ 1·8 = C.	40° F. — 32 (= 8) ÷ 1·8 = 4°·44 C.
C. × 1·8 + 32 = F. . . .	4°·44 C. × 1·8(= 8) + 32 = 40° F.

2. For temperatures *below* the zero of C. (32°), but not below the zero of F. (—17°·7 C.)

Rule.	*Examples.*
F. ~ 32 ÷ 1·8 = C. . .	20° F. ~ 32 (= 12) ÷ 1·8 = —6°·66 C.
—C. × 1·8 ~ 32 = F. . .	6°·66 C. × 1·8 (= 12) ~ 32 = 20 F.

3. For temperatures *below* the zero of F. (—17°.7 C.)

Rule.	*Examples.*
—F. + 32 ÷ 1·8 = —C. . .	20° F. + 32 (=52) ÷ 1·8 = —28°·8 C.
—C. × 1·8 ~ 32 = —F. . .	28°·8 C. × 1·8 (=52) — 32 = —29° F.

To convert Fahrenheit and Reaumur into each other, use the above rules, only substituting for C. 1·8, R. 2·5. $\frac{180}{80}=2·5$.

As the Centigrade thermometer is employed by all French and German writers on Chemistry, we subjoin for convenient reference a Table of the equivalent degrees of Centigrade and Fahrenheit between the freezing and the boiling points of mercury.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—40°	—40·0°	16°	60·8°	72°	161·6°	128°	262·4°	184°	363·2°
—39	—38·2	17	62·6	73	163·4	129	264·2	185	365·0
—38	—36·4	18	64·4	74	165·2	130	266·0	186	366·8
—37	—34·6	19	66·2	75	167·0	131	267·8	187	368·6
—36	—32·8	20	68·0	76	168·8	132	269·6	188	370·4
—35	—30·0	21	69·8	77	170·6	133	271·4	189	372·2
—34	—29·2	22	71·6	78	172·4	134	273·2	190	374·0
—33	—27·4	23	73·4	79	174·2	135	275·0	191	375·8
—32	—25·6	24	75·2	80	176·0	136	276·8	192	377·6
—31	—23·8	25	77·0	81	177·8	137	278·6	193	379·4
—30	—22·0	26	78·8	82	179·6	138	280·4	194	381·2
—29	—20·2	27	80·6	83	181·4	139	282·2	195	383·0
—28	—18·4	28	82·4	84	183·2	140	284·0	196	384·8
—27	—16·6	29	84·2	85	185·0	141	285·8	197	386·6
—26	—14·8	30	86·0	86	186·8	142	287·6	198	388·4
—25	—13·0	31	87·8	87	188·6	143	289·4	199	390·2
—24	—11·2	32	89·6	88	190·4	144	291·2	200	392·0
—23	— 9·4	33	91·4	89	192·2	145	293·0	201	393·8
—22	— 7·6	34	93·2	90	194·0	146	294·8	202	395·6
—21	— 5·8	35	95·0	91	195·8	147	296·6	203	397·4
—20	— 4·0	36	96·8	92	197·6	148	298·4	204	339·2
—19	— 2·2	37	98·6	93	199·4	149	300·2	205	401·0
—18	— 0·4	38	100·4	94	201·2	150	302·0	206	402·8
—17	+ 1·4	39	102·2	95	203·0	151	303·8	207	404·6
—16	3·2	40	104·0	96	204·8	152	305·6	208	406·4
—15	5·0	41	105·8	97	206·6	153	307·4	209	408·2
—14	6·8	42	107·6	98	208·4	154	309·2	210	410·0
—13	8·6	43	109·4	99	210·2	155	311·0	211	411·8
—12	10·4	44	111·2	100	212·0	156	312·8	212	413·6
—11	12·2	45	113·0	101	213·8	157	314·6	213	415·4
—10	14·0	46	114·8	102	215·6	158	316·4	214	417·2
— 9	15·8	47	116·6	103	217·4	159	318·2	215	419·0
— 8	17·6	48	118·4	104	219·2	160	320·0	216	420·8
— 7	19·4	49	120·2	105	221·0	161	321·8	217	422·6
— 6	21·2	50	122·0	106	222·8	162	323·6	218	424·4
— 5	23·0	51	123·8	107	224·6	163	325·4	219	426·2
— 4	24·8	52	125·6	108	226·4	164	327·2	220	428·0
— 3	26·6	53	127·4	109	228·2	165	329·0	221	429·8
— 2	28·4	54	129·2	110	230·0	166	330·8	222	431·6
— 1	30·2	55	131·0	111	231·8	167	332·6	223	433·4
0	32·0	56	132·8	112	233·6	168	334·4	224	435·2
+ 1	33·8	57	134·6	113	235·4	169	336·2	225	437·0
2	35·6	58	136·4	114	237·2	170	338·0	226	438·8
3	37·4	59	138·2	115	239·0	171	339·8	227	440·6
4	39·2	60	140·0	116	240·8	172	341·6	228	442·4
5	41·0	61	141·8	117	242·6	173	343·4	229	444·2
6	42·8	62	143·6	118	244·4	174	345·2	230	446·0
7	44·6	63	145·4	119	246·2	175	347·0	231	447·8
8	46·4	64	147·2	120	248·0	176	348·8	232	449·6
9	48·2	65	149·0	121	249·8	177	350·6	233	451·4
10	50·0	66	150·8	122	251·6	178	352·4	234	453·2
11	51·8	67	152·6	123	253·4	179	354·2	235	455·0
12	53·6	68	154·4	124	255·2	180	356·0	236	456·8
13	55·4	69	156·2	125	257·0	181	357·8	237	458·6
14	57·2	70	158·0	126	258·8	182	359·6	238	460·4
15	59·0	71	159·8	127	260·6	183	361·4	239	462·2

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
240°	464·0°	265°	509·0°	290°	554·0°	315°	599·0°	340°	644·0°
241	465·8	266	510·8	291	555·8	316	600·8	341	645·8
242	467·6	267	512·6	292	557·6	317	602·6	342	647·6
243	469·4	268	514·4	293	559·4	318	604·4	343	649·4
244	471·2	269	516·2	294	561·2	319	606·2	344	651·2
245	473·0	270	518·0	295	563·0	320	608·0	345	653·0
246	474·8	271	519·8	296	564·8	321	609·8	346	654·8
247	476·6	272	521·6	297	566·6	322	611·6	347	656·6
248	478·4	273	523·4	298	568·4	323	613·4	348	658·4
249	480·2	274	525·2	299	570·2	324	615·2	349	660·2
250	482·0	275	527·0	300	572·0	325	617·0	350	662·0
251	483·8	276	528·8	301	573·8	326	618·8	351	663·8
252	485·6	277	530·6	302	575·6	327	620·6	352	665·6
253	487·4	278	532·4	303	577·4	328	622·4	353	667·4
254	489·2	279	534·2	304	579·2	329	624·2	354	669·2
255	491·0	280	536·0	305	581·0	330	626·0	355	671·0
256	492·8	281	537·8	306	582·8	331	627·8	356	672·8
257	494·6	282	539·6	307	584·6	332	629·6	357	674·6
258	496·4	283	541·4	308	586·4	333	631·4	358	676·4
259	498·2	284	543·2	309	588·2	334	633·2	359	678·2
260	500·0	285	545·0	310	590·0	335	635·0	360	680.0
261	501·8	286	546·8	311	591·8	336	636·8		
262	503·6	287	548·6	312	593·6	337	638·6		
263	505·4	288	550·4	313	595·4	338	640·4		
264	507·2	289	552·2	314	597·2	339	642·2		

RULE FOR CALCULATING CHANGES OF VOLUME IN GASES BY PRESSURE.

The mean height of the barometer is to the observed height as the observed volume to the volume required, or the *mean pressure* (30 inches) is to the *observed pressure.* Hence, assuming 100 cubic inches of gas to be at 28 inches pressure: required the volume at 30 inches pressure.

Mean pr.		Obs. pr.		Observed volume.		Required volume.
30	:	28	: :	100	:	93.33

Thus 100 cubic inches are condensed to 93·33 cubic inches by the barometer rising two inches, from 28 to 30. The increase of pressure is 1-15th, and the diminution of volume is in the same proportion.

The increase in the *weight* of 100 cubic inches of gas at different pressures, may be determined by the following rule: if 100 cubic inches of gas weigh 30 grains, when the barometer is at 29 inches—required the weight at 30 inches.

Obs. pr.		Mean pr.		Observed weight.		Required weight.
29	:	30	: :	30	:	31·03

The pressure to which a gas, standing over mercury, is submitted, is indicated by the height of the barometer, when the mercury on the inside and outside of the vessel has the same level; but if the mercury on the inside be higher than on the outside, the difference in inches must be deducted from the height of the barometer, in order to obtain the exact pressure to which the gas is subjected.

RULE FOR CALCULATING CHANGES OF VOLUME IN GASES BY TEMPERATURE.

According to the researches of Gay-Lussac, 1000 volumes of air at 32° are increased to 1375 volumes at 212°. Hence the increase is $\frac{375}{180}$, or 2·08, for each degree between 32° and 212°: and 1000÷2·08=480. Hence the increase for each degree, is equal to 1-480th part of the volume at 32°; or, assuming that the volume of gas at this temperature is 480 cubic inches, there will be an addition of *one cubic inch* for every degree of increase in temperature up to 212°. By taking this as the proportionate increase at any two temperatures, it will be easy to calculate the change of volume for any other temperature. The mean temperature is taken at 60°, and 480 cubic inches at this temperature would become (60—32+480) 508 cubic inches. If the observed temperature be 70°, then 480 cubic inches at this temperature would be (70—32+480) 518 cubic inches. The number 32 is deducted from the temperatures because it is from this degree (32°) that the rate of expansion, on which the calculation is based, commences. It is obvious that it matters not whether the number 32 is deducted from the two temperatures, or from the number 480, as the sum will be the same in the two cases; but it makes this important difference in the calculation, that 480—32=448 furnishes a *constant*, which needs only to be added to each temperature, in order to produce the proportionate numbers. This constant is easily remembered, by the fact that the last figure of the three is produced by the addition of the two figures that precede it, each being equal to one half of the sum.

The rule for correction is, therefore, as follows: The increase at the observed temperature (70°) is to the increase at the mean temperature (60°) as the observed volume of gas (100 cubic inches) to the volume required, or

Obs. temp.		Mean temp.		Obs. vol.		Required vol.
448 + 70°	:	448 + 60°	::	100	:	98·069

Thus 100 cubic inches of gas at 70° are reduced in volume to 98·069 cubic inches by cooling 10°, *i. e.* from 70° to 60°. The rule may be represented under the following simple equation :—

$$\frac{448 + t' \times v}{448 + t} = x$$

t' Mean temperature.
t Observed temperature.
v Observed volume.

100 cubic inches at 40°. Required the volume at 60°. Answer: 448+60×100÷448+40=104·1.

With an alteration *in volume* there is an alteration *in weight*, and thus the difference at any two temperatures may be found by the following rule, in which observed weight is substituted for observed volume: Thus 100 cubic inches of air weigh 31 grains at 60°. Required the weight at 212°.

Obs. temp.		Mean temp.		Grs. obs. weight.		Required weight.
448 + 212°	:	448 + 60	::	31	:	23·86

AQUEOUS VAPOR IN GASES.

The subjoined Table represents the *proportion by volume* of aqueous vapor which exists in any gas, standing in contact with water at the corresponding temperatures and a mean barometric pressure. This must be deducted from the measured volume in order to determine the actual volume of any gas. (FARADAY.)

Temp.	A. V. by vol.	Temp.	A. V. by vol.	Temp.	A. V. by vol.
40°	·00933	54°	·01533	68°	·02406
41	·00973	55	·01585	69	·02483
42	·01013	56	·01640	70	·02566
43	·01053	57	·01693	71	·02653
44	·01093	58	·01753	72	·02740
45	·01133	59	·01810	73	·02830
46	·01173	60	·01866	74	·02923
47	·01213	61	·01923	75	·03020
48	·01253	62	·01980	76	·03120
49	·01293	63	·02050	77	·03220
50	·01333	64	·02120	78	·03323
51	·01380	65	·02190	79	·03423
52	·01426	66	·02260	80	·03533
53	·01480	67	·02330		

SPECIFIC GRAVITIES.

All bodies on the surface of the earth, are attracted towards its centre by *gravitation.* The comparative force with which gravitation acts on different bodies, is called their relative weight. Equal masses of the same substance gravitate equally; that is, have equal weights: but equal masses of different substances gravitate unequally; or, in other words, each species of substance has its own peculiar force of gravitation. *Specific gravity,* therefore, is the relative gravitating power (or weight) of equal volumes of different substances.

In determining specific gravities, two processes are necessary: first, that the substances compared should be reduced to equal volumes; secondly, that the comparative weight of these equal volumes should be found.

Specific Gravity of Liquids.—All *liquids* are easily reduced to equal volumes by filling the same bottle at the same temperature successively with each of them, and weighing it when so filled. These different weights, *minus* that of the bottle, are the comparative specific gravities of the liquids experimented on. The specific gravity of water, is the unit to which that of all liquids and solids is adjusted. The volume of liquids varies with their temperature, and that of 62° F. is generally adopted in this country as the standard.

Light glass bottles with perforated stoppers are sold, with a counterpoise, for the purpose of taking the specific gravities of liquids and small solids. They are so made that when counterpoised at 62°, they are calculated to hold from 100 to 1000 grains of pure (distilled) water. The specific gravity of a liquid is then at once determined by its weight. Thus the 1000-grain bottle would hold 796 grains of absolute alcohol (0·796), and 1846 grains of concentrated sulphuric acid (1·846). In delicate experiments it is always advisable to take the exact weight of water which the counterpoised bottle will hold; as slight differences in the volume, and therefore in the weight of water, arise from fluctuations in temperature. Thus, according to the temperature, the bottle will sometimes hold more and sometimes less than 1000 grains.

In pathological researches, it is occasionally required to take the sp. gr. of a very small quantity of liquid. A light glass tube about three inches long, and about three-eighths of an inch in diameter, may be employed for this purpose. It may be fixed in a hole in a cork, and accurately balanced. It should be marked in horizontal lines, at different levels, by a diamond; and the weight of distilled water at any one of these levels being ascertained, the weight of the liquid at the same level may be afterwards determined. The two weights will, by the rule of proportion, give the specific gravity.

Baumé's *hydrometer* is much used on the Continent. We subjoin a Table, in which the degrees of this hydrometer are compared with the ordinary range of the specific gravities of liquids.

FOR LIQUIDS HEAVIER THAN WATER.

Degrees.	Sp. gravity.	Degrees.	Sp. gravity.	Degrees.	Sp. gravity.	Degrees.	Sp. gravity.
0	1·000	20	1·152	40	1·357	60	1·652
1	1·007	21	1·160	41	1·369	61	1·670
2	1·013	22	1·169	42	1·381	62	1·689
3	1·020	23	1·178	43	1·395	63	1·708
4	1·027	24	1·188	44	1·407	64	1·727
5	1·034	25	1·197	45	1·420	65	1·747
6	1·041	26	1·206	46	1·434	66	1·767
7	1·048	27	1·216	47	1·448	67	1·788
8	1·056	28	1·225	48	1·462	68	1·809
9	1·063	29	1·235	49	1·476	69	1·831
10	1·070	30	1·245	50	1·490	70	1·854
11	1·078	31	1·256	51	1·505	71	1·877
12	1·085	32	1·267	52	1·520	72	1·900
13	1·094	33	1·277	53	1·535	73	1·924
14	1·101	34	1·288	54	1·551	74	1·949
15	1·109	35	1·299	55	1·567	75	1·974
16	1·118	36	1·310	56	1·583	76	2·000
17	1·126	37	1·321	57	1·600		
18	1·134	38	1·333	58	1·617		
19	1·143	39	1·345	59	1·634		

FOR LIQUIDS LIGHTER THAN WATER.

Degrees.	Sp. gravity.	Degrees.	Sp. gravity.	Degrees	Sp. gravity.	Degrees.	Sp. gravity.
10	1·000	23	0·918	36	0·849	49	0·789
11	0·993	24	0·913	37	0·844	50	0·785
12	0·986	25	0·907	38	0·839	51	0·781
13	0·980	26	0·901	39	0·834	52	0·777
14	0·973	27	0·896	40	0·830	53	0·773
15	0·967	28	0·890	41	0·825	54	0·768
16	0·960	29	0·885	42	0·820	55	0·764
17	0·954	30	0·880	43	0·816	56	0·760
18	0·948	31	0·874	44	0·811	57	0·757
19	0·942	32	0·869	45	0·807	58	0·753
20	0·936	33	0·864	46	0·802	59	0·749
21	0·930	34	0·859	47	0·798	60	0·745
22	0·924	35	0·854	48	0·794	61	0·741

TWADDELL'S *hydrometer* is employed by English Chemical manufacturers. The degrees on Twaddell, are readily converted into equivalent specific gravities, by multiplying them by 5, and adding 1000. Thus 8° Twaddell, $8 \times 5 = 40 + 1000 = 1040$. We subjoin a Table of their equivalents.

Degrees.	Sp. gravity.	Degrees.	Sp. gravity.	Degrees.	Sp. gravity.	Degrees.	Sp. gravity.
1	1·005	8	1·040	15	1·075	22	1·110
2	1·010	9	1·045	16	1·080	23	1·115
3	1·015	10	1·050	17	1·085	24	1·120
4	1·020	11	1·055	18	1·090	25	1·125
5	1·025	12	1·060	19	1·095	26	1·130
6	1·030	13	1·065	20	1·100	27	1·135
7	1·035	14	1.070	21	1·105	28	1·140

SPECIFIC GRAVITY OF POWDERS OR SMALL SOLIDS.—The sp. gr. of *solids in powder or in small pieces* may also be conveniently determined by a bottle. Thus: weigh the powder, pour it into the bottle, and fill it with water at 62° F., taking care to dislodge all adhering bubbles of air. Then weigh it and deduct the known weight of the bottle: the remainder is the conjoint weight of the powder and water. Deduct from this last sum the found weight of the powder, and the difference is the weight of the water; deduct this difference from the known weight of water, required to fill the bottle, and the remainder is the weight of a volume of water, equal to the volume of the solid in powder; then, as this is to the known weight of water, required to fill the bottle : : sp. gr. water : sp. gr. powder.

We subjoin an example in reference to *native platinum* in grains:—

	Grains.
Weight of water in the bottle	1000
Weight of native platinum grains (in air)	40
	1040
Weight of water and platinum in bottle	1037·5
Difference = vol. of water displaced	2·5

40 ÷ 2·5 = 16 sp. gr. of native platinum.

The sp. gr. of mercury, or any liquid or solid, not dissolved by water, may be obtained by the same rule. When the substance is soluble in water, another liquid of known sp. gr., which does not act upon the solid, must be employed. Alcohol, oil of turpentine, or olive oil, may be used, or, in some cases, the substance may be coated with varnish. Assuming that the sp. gr. of *sugar* is required, and the liquid selected is oil of turpentine, sp. gr. 0·870; the sugar is first weighed in air, and then in the oil; the difference gives the weight of an equal bulk of the oil; then, if the weight of the sugar in air be 400 grains, and its weight in oil of turpentine 182·5, the weight of an equal bulk of the oil, will be 400—182·5=217·5. Then 0·870 : 1000 : : 217·5 : 250, and 400÷250=1·6, which is the sp. gr. of the sugar.

Specific Gravity of Solids Heavier than Water.—Weigh the solid in air, then suspend it by a fine thread to one arm of a balance; exactly counterpoise it, and immerse the solid so counterpoised in distilled water at 62° F., and note how much less it weighs now, than when weighed in air. The difference between the two, is the weight of a volume of water, exactly equal to that of the immersed solid. Divide the weight of the solid in air by this difference, and the result is the sp. gr. of the solid. Thus in reference to a small bar of aluminum:—

	Grains.
Weight of aluminum in air	46·3
Weight of aluminum in water	29·0
Difference = volume of water	17·3

46·3 ÷ 17·3 = 2·6 sp. gr. of aluminum.

A portion of bone in air, weighed 90·6 grains: in water 45·6. Difference=45 grains; and 90·6÷45=2·01 sp. gr. of *bone*. A portion of muscle weighed in air, 91·2 grains: in water 7·2 grains. Difference=84 grains; and 91·2÷84=1·085 sp. gr. of *muscle*.

A knowledge of the specific gravity of solids, enables a chemist to determine the weight of bodies from their volume. A cubic foot of water contains 1728 cubic inches, and weighs 1000 ounces (strictly, 998 ounces or 62·4 pounds Av.); hence a cubic foot of sulphur (sp. gr. 1·957) would weigh 1957 ounces, and a cubic foot of marble (sp. gr. 2·5) would weigh 2500 ounces. A cubic foot of ice weighs 937·6 ounces, or 58·6 pounds Av.; a cubic foot of air weighs 535·161 grains.

Specific Gravity of Solids Lighter than Water.—1. Find the weight of the solid (*a*) in air. 2. Take a piece of metal heavy enough to make *a* sink in water, and find its weight in air and in water. 3. Tie together *a* and the metal, and find the weight of the compound mass in water. The difference between the weight of the metal in air and in water, is the weight of a volume of water, equal to that of the metal; deduct this from the difference between the weights in air and in water of the compound mass, and the remainder is the weight of a volume of water equal to *a*. We divide the weight of *a* by the remainder, and obtain the sp. gr. Thus with reference to beef-fat:—

	Grains.
Weight of the fat in air	117·3
Add brass weight to sink it	1000·0
Weight of compound mass in air	1117·3

	Grains.
Loss of weight by the compound mass in water	245·5
" brass weight (1000) "	119·4
Weight of the water displaced by the fat	126·1

Hence 117·3 ÷ 126·1 = 0·930 sp. gr. of beef-fat.

Specific Gravity of Gases.—The principles are the same as those above described for determining the specific gravity of solids and liquids. The weighing of the air and gas, should take place at the same temperature and pressure, or a calculation should be made according to the rules already given (p. 672). In reference to Gases and Vapors, *air* is taken as the standard of unity (pp. 77 and 680).

Gases.—A light glass flask, of about 40 or 50 c. i. capacity, is employed. This is capable of being screwed to the air-pump plate, and of being suspended to a scale-beam and accurately balanced. The flask is exhausted, balanced, filled with dry air, and again balanced. The increase in weight represents the weight of the volume of dry air in the flask, at the pressure and temperature, at which it was filled. The experiment is repeated with the dry *gas*, the sp. gr. of which it is proposed to determine. The following is an example of the sp. gr. of Carbonic acid:—

	Grains.
Weight of the flask with dry air	2033·8
Weight of the flask exhausted	2021·4
Weight of dry air in the flask	12·4

	Grains.
Weight of the flask with dry carbonic acid	2040.24
Weight of flask exhausted	2021·40
Weight of dry carbonic acid in flask	18·84

Hence 18·84 ÷ 12·4 = 1·520 sp. gr. of carbonic acid.

When the sp. gr. of a gas has been ascertained, the weight of 100 cubic inches is determined by multiplying the sp. gr. of the gas by the weight of 100 cubic inches of air =31 grains (pp. 145 and 680). Thus, 100 cubic inches of dry carbonic acid, are found by experiment to weigh 47·08 grains, and its sp. gr. (1·520×31=47·1) gives 47·1 grains for the weight of 100 cubic inches, calculated by this rule. Conversely, when we have ascertained the weight of 100 cubic inches of a gas, we can determine its sp. gr. by dividing this weight by 31. Thus 47·1÷31=1·520. The sp. gr. of a gas, of which the atomic weight is known, may also be determined, by multiplying the atomic weight by the sp. gr. of hydrogen. Thus the atomic weight of carbonic acid is 22, and 22×·0691=1·5202, the sp. gr. of carbonic acid. On the other hand, if the sp. gr. is known, the atomic weight may be determined by dividing the sp. gr. of the gas, by the sp. gr. of hydrogen, thus 1·502÷0691=22, the atomic weight of carbonic acid. When however the atomic weight of a gas corresponds to 2 volumes then the quotient must be divided by 2, to obtain the real sp. gr. Thus in reference to ammonia, the atomic weight is 17, and 17×·0691=1·1747. As the atom of ammonia corresponds to 2 volumes, then 1·1747÷2=·5873, sp. gr. of ammonia.

A knowledge of the sp. gr. of gases, enables a chemist to control the results of an analysis of a compound gas. Thus if 2 volumes of ammonia consist of 1 volume of nitrogen and 3 volumes of hydrogen, it follows that the sum of the specific gravities of its constituents, divided by 2, should exactly represent the sp. gr. of the gas. (*See* p. 168, also p. 680.)

SPECIFIC GRAVITY OF VAPORS.—The determination of the sp. gr. of vapors is attended with greater practical difficulties, but the principle of the operation is the same. We compare the weights of equal volumes of the vapor and air under the same temperature and pressure. A thin glass globe of about three inches diameter is drawn out at its neck to a narrow tube, six or seven inches long, the point of the tube being cut across with a file, but not sealed. The globe is then weighed, and the temperature and pressure at the time are observed. In order to introduce the volatile liquid, the globe is warmed so as to expel a portion of its air, and the end of the tube is then dipped into the liquid. As the globe cools, the air within contracts, and the liquid is forced into it by atmospheric pressure. When a sufficient quantity (from 100 to 150 grains) of liquid has entered, the globe is firmly inclosed in a wire holder, and immersed in a bath of water, oil, or other medium, heated to 50° or 60° above the boiling-point of the liquid in the globe. Under these circumstances, a stream of vapor rushes rapidly through the orifice, carrying with it the air of the globe. When this ceases, the point of the tube is sealed by a blowpipe flame, the temperature of the bath being observed at the same moment. The globe is removed from the bath, and when cool is cleaned and weighed.

The next point to be determined is the *capacity* of the globe. For this purpose the neck is broken under the surface of water or mercury, when the cold fluid enters the globe and fills it completely, if the operation has been properly conducted, and all the air has been expelled by the vapor. By pouring out the water or mercury into a graduated vessel, the capacity of the globe is accurately ascertained. We thus obtain the data necessary for the calculation.

1. The weight of the globe full of air at the common temperature and pressure.

2. The weight of the globe, and of the vapor filling it at the temperature of the bath, and under the same pressure.

3. The capacity of the globe. Having these results, we obtain by calculation—

4. The weight of the empty globe.

5. The weight of the vapor filling the globe at the temperature of the bath, as well as its volume at this or any other temperature that may be required.

Let it be assumed that the object is to determine the specific gravity of the vapor of *Chloroform*. 1. The weight of the globe full of air at 60° and bar. 30, is found to be 2012·4 grains. 2. The liquid chloroform having been introduced into the globe, in the manner described, the globe is maintained at a temperature of 200° in the bath, until nothing but vapor remains in the interior. The aperture of the small tube is then sealed. The globe, when dry, and cooled at 60°, is found to weigh 2040 grains. This gives the weight of the globe and vapor together. 3. The capacity of the globe is determined by breaking the point of the tube under water. The liquid rushes in and entirely fills the vessel. When this liquid is poured into a graduated glass, it is found that at 60° there are 40 cubic inches; hence, 40 cubic inches of air were contained in the globe at common temperature and pressure. 4. The weight of this air would be 12·4 grains (100 c. i. : 31 grs. : : 40 c. i. : 12·4 grs.) : and as the globe and air weighed together 2012·4 grains, then 2012·4—12·4=2000 grains, the weight of the empty globe. 5. The weight of the *vapor* filling the globe may now be determined. The globe was found to weigh, on cooling, 2040 grains, hence, 2040—2000=40 grains, the weight of the vapor. It is now necessary to determine either the weight of air which would fill the globe at the temperature of the bath, or the volume of vapor which by calculation would be contained in the globe when cooled at 60°. The reduction of the volume by cooling from 200° to 60° is the more simple process. Thus, 40 cubic inches of vapor at 200° would be reduced to 30·78 cubic inches at 60° (648 : 508 : : 40 : 30·78 (p. 673). Hence, assuming that chloroform vapor was cooled to 60°, and could still exist as vapor at that temperature, it is obvious that its specific gravity would be determined by ascertaining the weight of 30·78 cubic inches of air at the same temperature and pressure. 100 cubic inches of air weigh 31 grains, hence 100 : 31 : : 30·78 : 9·54. Hence, at the same temperature, 60°, 30·78 cubic inches of chloroform would weigh 40 grains, while an equal volume of air would weigh only 9·54 grains; and 40÷9·54=4·19, which is nearly the specific gravity of the vapor of chloroform, as determined by calculation from its elementary composition. We subjoin a summary of these results:—

Capacity of the globe at 60° = 40 cubic inches.
Weight of the globe with dry air = 2012·4 grains.
Weight of the air by calculation = 12·4 grains.
Weight of the globe without air = 2000 grains.
Weight of the globe with chloroform vapor = 2040 grains.
Weight of the chloroform in vapor = 40 grains.
40 c. i. of air or vapor at 200°, reduced to 30·78 c. i. at 60°.
Weight of 30·78 c. i. of air at 60° = 9·54 grains.
Weight of 30·78 c. i. of chloroform vapor at 60° = 40 grains.

Hence—

Wt. of air.		Wt. of chlor. v.		Sp. gr. air.		Sp. gr. chr. v.
9·54	:	40	: :	1·000	:	4·192

It may be observed that the ascertained sp. gr. of chloroform-vapor is 4·20; and the sp. gr. of the vapor calculated from its elementary composition, is 4·1805, differences which are comparatively unimportant (p. 518).

The relations of sp. gr. to weight and volume, are the same with vapors, as with gases. In fact, all the conditions which affect gases, equally affect vapors, so long as these bodies have a temperature above the boiling-points of the liquids which produce them.

The weight of 100 cubic inches of the vapor of water, may be determined from its sp. gr. by the rule already given (p. 677). Thus 0·6129×31=19·27 grains. The sp. gr. of the vapor of arsenic being 10·39, 100 cubic inches of this vapor would weigh 322·09 grains (10·39×31).

A determination of the specific gravity of vapors or of vapor-density, is of considerable importance in the analysis of volatile organic liquids. There are many liquid hydrocarbons which, so far as centesimal composition is concerned, yield precisely similar weights of hydrogen and carbon, by the combustion-tube. The specific gravity of their vapors, however, differs; and this difference often enables a chemist to apportion with great accuracy their atomic constitution. The sp. gr. of a compound vapor must always be the sum of the sp. gr. of its constituent elements, or a multiple of them. We need not go further into this subject, as the reader will find several examples given at p. 517.

TABLE OF SIMPLE AND COMPOUND GASES AND VAPORS.

Gases and vapors.	Symbols.	Atom Vol.	Atomic Weight.	Sp. gr. of air 1.	Sp. gr. of hydrogen 1.	Weight of 100 c. i. in grains.
Air	....	...	...	1·000	14·48	31·00
Hydrogen	H	1	1	0·0691	1·	2·14
Oxygen	O	$\frac{1}{2}$	8	1·1057	16·	34·24
Nitrogen	N	1	14	0·9674	14·	29·96
Chlorine	Cl	1	36	2·4876	36·	77·04
Bromine	Br	1	78	5·3898	78·	166·92
Fluorine	F	1 ?	19	....	19·	
Iodine	I	1	126	8·7066	126·	269·64
Sulphur	S	$\frac{1}{6}$	16	6·6336	96·	205·44
Selenium	Se	$\frac{1}{6}$	40	16·6390?	240·	515·80
Phosphorus	P	$\frac{1}{2}$	32	4·3555	64·	136·96
Carbon	C	1 ?	6	0·4146	6·	12·84?
Tellurium	Te	$\frac{1}{6}$	64	4·4190	38·4	136·98
Arsenic	As	$\frac{1}{2}$	75	10·3900	150·	322·09
Aqueous vapor	HO	1	9	0·6219	9·	19·26
Protox. of nitrogen . . .	NO	1	22	1·5202	22·	47·08
Deutox. of nitrogen . . .	NO_2	2	30	1·0365	15·	32·10
Nitrous acid	NO_4	1	46	1·5890	46.	49·15
Ammonia	NH_3	2	17	0·5873	8·5	18·19
Hypochlorous acid	ClO	1	44	3·0404	44·	94·16
Peroxide of chlorine . . .	ClO_4	2	68	2·3494	34·	72·76
Hydrochloric acid	HCl	2	37	1·2783	18·5	39·59
Hydrobromic acid	HBr	2	79	2·7294	39·5	84·53
Hydriodic acid	HI	2	127	4·3878	63·5	135·89
Hydrofluoric acid	HF	2 ?	20	....	10·	
Sulphurous acid	SO_2	1	32	2·2112	32·	68·48
Hydrosulphuric acid . . .	HS	1	17	1·1747	17·	36·38
Hydroselenic acid	HSe	1	41	2·7950	41·	86·64
Phosph. hydrogen	PH_3	2	35	1·1925	17·5	36·96
Terchlor. of phosph. . . .	PCl_3	2	140	4·7420	70·	147·00
Pentachl. of phosph. . . .	PCl_5	4	212	3·6600	53·	113·46
Carbonic oxide	CO	1	14	0·9674	14·	29·96
Carbonic acid	CO_2	1	22	1·5202	22·	47·08
Light carb. hydrogen . . .	CH_2	1	8	0·5528	8·	17·12
Olefiant gas	C_2H_2	1	14	0·9674	14·	29·96
Cyanogen	NC_2	1	26	1·7966	26·	55·64
Hydrocyanic acid	HCy	2	27	0·9328	13·5	28·89
Tellur. hydrogen	TeH_3	1	65	4·4881	65·	139·11
Arsen. hydrogen	AsH_3	2	78	2·7010	39·	83·73
Alcohol	$C_4H_6O_2$	2	46	1·6100	23·	49·91
Ether	C_4H_5O	1	37	2·5567	37·	80·25
Chloroform	C_2HCl_3	2	121	4·1805	60·5	129·59
Oil of turpentine	$C_{20}H_{16}$	2	136	4·6980	68·	145·63

[The reader is referred to page 63 for a table of the symbols and atomic weights of the ELEMENTS. Tables, showing the proportion per cent. of dry acids and alkalies, as well as of alcohol with water, will be found in their proper places in the body of the work.]

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